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STUDY OF REACTIONS OF SULFUR IN STACK PLUMES

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FIRST ANNUAL REPORT

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discussed in this report

I. SUMMARY

The results of the first year's effort of a projected three-year study of the reactions of sulfur in stack plumes are presented in this report.

The overall objective of this program is to provide an improved rationale for predicting the concentration levels of sulfur oxides in the atmosphere. To attain this objective, it is necessary to define those chemical and/or physical processes which contribute to the loss or alteration of sulfur compounds as a function of plume composition, environmental variables and source parameters.

The study ~~has been~~ was divided into two major phases; (a) a field program in which real plumes from coal and oil-fired power stations can be tracked by aircraft to determine plume composition as a function of downwind distance, environmental factors and source parameters; and (b) a laboratory program in which flue gas effluents generated by a pilot plant furnace (oil and coal fired) can be studied under simulated field conditions. Bench scale experiments to investigate several alternative mechanisms (chemical and/or physical) contributing to observed SO_2 losses in the atmosphere are also included in the first-year program. Two Boston area power plants, one coal fired and the other oil fired, are cooperating in this study by allowing measurement of source parameters. The selected coastal stations are located such that no interference between their respective plumes (or other recognized SO_2 sources) takes place during periods of off-shore winds.

Plume sampling was conducted insofar as possible under pre-selected meteorological conditions which would allow for maximum plume stability, low wind velocity, approximately 10 mph, inversion or near-neutral conditions with shallow mixing depth, and travel over water to minimize turbulence effects. During the period covered by this report, 10 flights were made for plume sampling, plume mapping, and instrument calibration purposes.

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Plume location beyond the visible range was determined by an automatic conductivity analyzer. This technique enabled mapping of plume boundaries for distances up to 12 miles while simultaneously furnishing SO_2 concentration values as a function of downwind distance. Downwind samples were also collected by aircraft for SO_2 and SO_3 by filters and midget impingers. Limited measurements during this period showed that the experimental techniques were satisfactory and that the SO_2 concentration values were within the expected range for the existing meteorology. Sulfur hexafluoride, SF_6, was injected at the base of each power plant stack as a conservative tracer. By comparing the downwind concentration ratios of SO_2 and SF_6 with their known source values, an indication of SO_2 reactions in the atmosphere will be furnished. The development of final instrumentation to accomplish these measurements is now in progress.

A pilot plant combustion system was designed by Riley Stoker Corporation and installed and calibrated at the GCA Bedford laboratories during this period. This equipment, operating at the 50,000 BTU per hour level, produces real flue gas effluents from the combustion of either No. 6 oil or pulverized coal.

A 42-ft^3 reaction chamber was constructed to investigate atmospheric behavior of SO_2 from stack plumes under controlled temperature, humidity, and simulated solar irradiation. Synthetic gas mixtures or real effluents from the pilot plant furnaces can be introduced into this chamber to study SO_2 decay under simulated field conditions. Preliminary analyses have been made by IR spectroscopy on synthetic SO_2 air mixtures in the chamber as part of the sampling instrument development and system calibration.

Bench scale experiments were performed in which quantum yields were determined for pure SO_2 and mixtures of SO_2 and O_2 for various uv excitation levels, 2537 and 3100Å, at ambient pressure. Test results were in general agreement with previous quantum yields cited in the literature. Extrapolation of data to the low concentration ranges to be examined later in this program suggests that the uncatalyzed homogeneous photochemical formation of SO_3 may attain the significant level of 2.4 percent per hour. The above value was based upon a quantum yield of 0.04 for 3130Å irradiation of SO_2 at the 1 to 10 ppm level.

II. INTRODUCTION

GCA Technology Division has completed the first year of a projected three-year study of "Reactions of Sulfur in Stack Plumes" under Contract No. PH-86-67-125, supported jointly by the Public Health Service, National Air Pollution Control Administration; American Petroleum Institute; Bituminous Coal Research, Inc.; and the Edison Electric Institute. Progress to date is presented in this First Annual Report.

During the period covered by this report, two technical presentations were delivered based upon the study. The first, which was given at the Annual Meeting of the Air Pollution Control Association, New England Section, held at Providence, Rhode Island, on April 5, 1967, was entitled "Reactions of Sulfur Oxides in Stack Plumes" (scope and design of study). A second presentation, of the same title and discussing preliminary studies, was made at the Annual Meeting of the American Industrial Hygiene Association, New England Section, held at Hartford, Connecticut, in November, 1967.

The overall objective of the three-year program is to provide an improved rationale for predicting the concentration levels of sulfur compounds in the atmosphere. The emphasis in this study is directed to the physical and/or chemical reactions of sulfur compounds in fossil fuel combustion gases during or after release to atmosphere which must be considered in the development of useful meteorological diffusion models. The scope of this program has been constrained mainly to the investigation of those chemical and physical processes leading to the conversion of sulfur dioxide to sulfur trioxide and sulfuric acid, since these compounds are the major constituents in most polluted atmospheres.

In order to meet the program objectives, both field and laboratory experiments have been incorporated in the research plan. The field approach defines the composition changes in real fossil fuel effluents from stack source to extended downwind travel distances by measurement of stack and plume SO_x concentrations and associated meteorological parameters. Laboratory experiments with fossil fuel stack effluents and synthetic gas mixtures have been designed to permit detailed studies of those physical and chemical reactions believed to occur in stack plumes.

The analysis of field measurements, which depict the proper order of plume concentration levels despite statistical limitations, and supporting laboratory data, which permit improved resolution of system variables, is intended to furnish a better understanding of the behavior of sulfur oxides in the atmosphere.

The research program consists of two major phases each divided into two tasks:

Phase I - Field Studies

Task 1. Source sampling
Task 2. Aircraft plume sampling

Phase II - Laboratory Studies

Task 3. Pilot plant flue gas facility and chamber reaction studies
Task 4. Chemical reaction kinetics studies

The field studies, Phase I, are designed to determine source strengths, Task 1, for sulfur oxides and particulate emissions from coal and oil-fired power boilers while operating at full load and under meteorological conditions selected to optimize sampling procedures. Concurrent sampling of the plume at several downwind locations by aircraft-borne instrumentation, Task 2, is intended to provide comparative measurements of diluted plume constituents. By adding conservative tracer materials which do not ordinarily undergo chemical changes in the atmosphere, the observed relative decay of SO_2 and tracer will provide a basis for distinguishing between simple meteorological dilution and chemical reactions within the plume.

The laboratory studies, Phase II, are designed both to supplement and confirm field observations whenever practical, Task 3, and to furnish key data on chemical reaction kinetics not currently available, Task 4. Construction of a pilot plant flue gas generating facility with which typical combustion effluents from sulfur-bearing residual oils or pulverized coals can be studied under simulated field conditions in a special reaction chamber constitutes the Task 3 effort. Provisions for irradiating the chamber (stirred reactor) contents (both flue gases and synthetic gas mixtures) under a controlled range of simulated environmental conditions, e.g., gas composition, concentration level, temperature, humidity, and irradiation level will supplement and refine field observations. Task 4 of the experimental program, will include laboratory studies of critical reaction rates relating to catalytic and photolytic processes and certain aspects of the chemical kinetics identified as significant.

The overall research program is designed to provide sufficient data on chemical loss rates to permit calculation of the downwind concentrations of the oxides of sulfur in stack plumes over distances of the order of 25 miles or more. It is assumed here that source location, intensity and key meteorological parameters are appropriately defined.

In order to achieve the overall objectives of the three-year study, the following goals were set for the first year's program schedule: (1) Construction of a pilot plant combustion system to provide realistic effluents; (2) installation of a stirred reactor for investigation of plume SO_2 loss kinetics; (3) completion of initial laboratory studies to determine critical reaction rates, chiefly photochemical; and

(4) completion of initial field studies to define source strengths, select and prove out ground and aerial instrumentation and obtain initial plume concentrations and SO_2 decay rates.

The progress which has been made in each of the above major tasks is described in the following sections of this report. The only major problem arising during the first year was the inadequacy of particulate phosphor tracers as a means of tracking invisible plumes. In view of the added time required to develop a satisfactory plume tracking system, a large fraction of the first year field effort was reassigned to the second year program. With the exception of a minor delay in the installation of the stirred reactor, the objectives of the remaining first year's tasks have been achieved.

To provide the broad technical base required for this program, GCA Technology Division has collaborated with other research organizations for certain special services.

Major technical disciplines and responsible contractor groups are listed in the following tabulation:

Discipline	Contractor
(1) Analytical Chemistry	GCA Technology Division Bedford, Massachusetts
(2) Meteorology	
(3) Photochemistry	
(4) Stack Measurements	
(5) Stirred Reactor	
(6) Program Management	
(7) Pilot Combustion Plant Design and Construction	Riley Stoker Corporation Worcester, Massachusetts
(8) Power Plant Technology	
(9) Flight Program	Singco Dept., Bolt, Beranek, and Newman, Inc. Cambridge, Massachusetts

III. FIELD STUDIES - SOURCE STRENGTH MEASUREMENTS OF SULFUR OXIDES

A. TEST PROGRAM

The objectives of the source measurements program, Task 1, are (1) to determine the effluent concentrations of large power boilers fueled with coal and oil, respectively, for constituents presumed to be of importance in the loss of SO_2 from the downwind plume; (2) to add to the plume simultaneously a known amount of inert sulfur hexafluoride (SF_6) tracer material; and (3) to measure those plant operating factors, i.e., volume flow rate, velocity and exit temperature of the combustion gas, load level, fuel composition and stack height, which determine the overall plume characteristics.

Since the above measurements establish source strengths for SO_2 and SF_6 emissions, any differences in the relative decay rate for these materials as determined by concurrent aircraft plume sampling, are evidence of SO_2 depletion processes. Analysis of the flue gas for fly ash concentration and composition coupled with measurement of such environmental factors as temperature, humidity, and solar flux levels provide a means for deducing which mechanisms control SO_2 losses. Details on aircraft sampling procedures and other factors not directly related to the stack sampling phase of this study are presented in later sections of this report.

B. TEST LOCATIONS AND PROCEDURES

In order to carry out effectively the several field measurements associated with this program, it was imperative that power stations (flue gas source) be (a) located within reasonable travel distance, < 1 hour, from a central laboratory facility, (b) that both coal and oil fired facilities be available so that differences in effluent composition and behavior could be studied, (c) that both power stations be exposed to essentially the same meteorological regime, (d) that the power levels, stack heights and exit gas temperatures of both plants be comparable, and (e) that no significant admixture of plumes from the selected stations (or other major pollutant sources) should take place.

Aside from the fact that the power stations should be in the same climatological region, it was also desired that the topography be restricted to moderately level terrain with no hills or valleys to divert the plume or engender turbulence during its downwind travel. The two cooperating power plants described below satisfy the above criteria provided that measurements are confined to periods when the wind is from the southwest to northwest direction. In both cases, this leads to plume travel over water and beyond the flight patterns of commercial air traffic.

In order to facilitate plume tracking and sampling, a very stable, near inversion regime with low wind velocities, 8 to 10 mph, and shallow mixing depths, < 2500 ft, are desired. Under these conditions, vertical diffusion is reduced and the plume pursues a regular course for extended distances with minimal dilution of components. Such weather conditions are associated with the fall and spring inversions forming a classic part of the climatology in the eastern Massachusetts area. Further details of the meteorological aspects of this study are discussed in Section IV and VIII.

Two Massachusetts Public Utility systems are cooperating in this study by allowing the sampling of flue gas constituents prior to discharge. Locations of the two stations are shown in Figure 1. The Boston Edison Company, Edgar Station (oil) is located on the east shore of the Weymouth Fore River adjacent to Quincy Bay in Weymouth, Massachusetts, approximately 9 miles SSE of Boston. This plant has three, 90-MW units, each with 266-foot stacks (MLW) and an older complex aggregate of some 80 MW. Total full load capacity is approximately 350 MW.

At the Edgar Station, three equispaced sampling ports are located in the paired 6 by 12 ft. high breechings connecting to each stack. The results of velocity traverses in the center (C) and lower(L) ports are given in Table 1. Static pressure in these breechings was positive at approximately 1 inch of water gage.

The New England Electric System Salem Harbor Station (coal) is located in Salem, Massachusetts, on the west shore of Salem Harbor, approximately 15 miles NNE of Boston. It has two units of 85 MW (Unit Nos. 1, 2; 1952) and one unit of 150 MW (Unit No. 3, 1958), with three 270-foot stacks, (MLW).

Each unit at the Salem Harbor Station has two breechings which lead from an electrical collector to two induced draft fans and then to a single stack. A single centerline sampling port is located on the side of each rectangular breeching (4.75 by 5.5 feet high) between the induced draft fan and the stack. Centerline breeching velocities determined by a six-point pitotstatic traverse were approximately 10 percent higher than the average velocities shown in Table 1. The centerline values were used to attain isokinetic sampling conditions for particulates. Static pressures at the sampling points were less than 1 inch water gage, negative.

Pertinent information on source characteristics of the Salem and Edgar Stations are given in Table 2. Gas flow rates as measured at the Edgar Station are in good agreement with Table 2 data. The fact that current measurements of gas flow rates at Salem Harbor, Table 1, exceed those shown in Table 2 is attributed to skewness in velocity profiles. Had a complete traverse been possible, it is believed that average velocities would have agreed closely with those calculated on the basis of fuel consumption and air-to-fuel ratio.

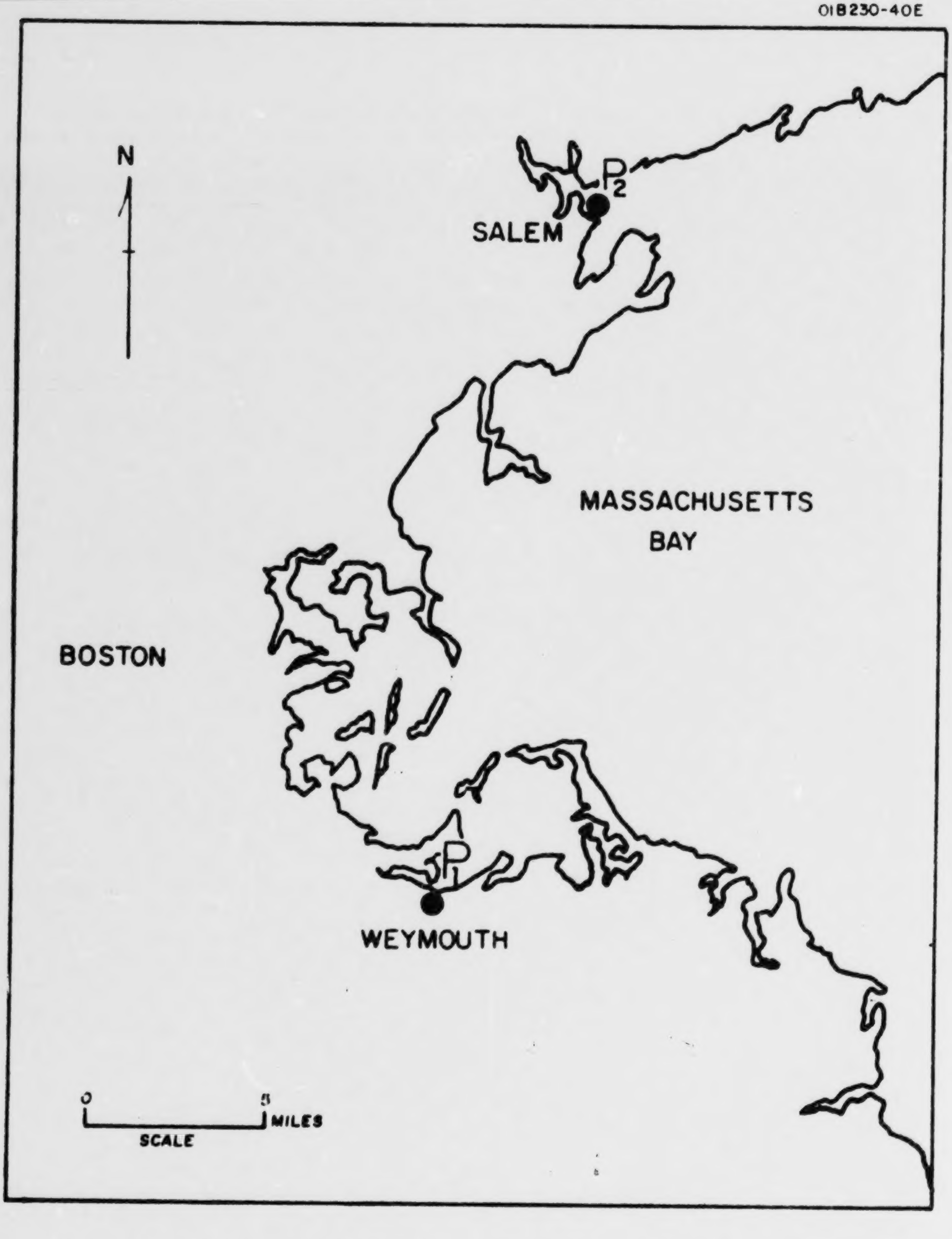
01B230-40E
N
SALEM
P_2
MASSACHUSETTS
BAY
BOSTON
P_1
WEYMOUTH
0
5
MILES
SCALE

Figure 1. Location and power plants for initial field tests. Plant P_1 is oil fired; plant P_2 is coal fired.

TABLE 1

MEASURED GAS FLOWS IN BREECHINGS AT SALEM HARBOR AND EDGAR STATIONS

Station	Unit	Breeching	Gas Flow (cfm)	Total	Velocity (fpm)	Temp. (^oF)
Salem Harbor	1	1	151000		5780	290
		2	142500		5460	260
				293500		
	2	1	157000		6000	280
		2	167800		6425	290
				324800		
	3	1	226000		8680	260
		2	208000		7950	
				434000		
Edgar	10	1L			1600	290
		1C	115920		1620	
		2L			2180	300
		2C	151200		1920	
				267120		
	11	1L			2050	300
		1C	149400		2100	
		2L			2060	290
		2C	148680		2070	
				298080		

TABLE 2

DATA FROM SALEM HARBOR AND EDGAR STATIONS

SALEM

Stack Height — all three are 250 ft from ground and 270 ft 6 in. from mean low water (MLW)

Stack Inside Diameters —

Units	Bottom	Top
1 and 2	13 ft	10 ft 6 in.
3	16 ft	13 ft

Fuel Consumption at Full Load —

Unit	Ton coal/hr (13,400 BTU/lb)
1	28.8
2	29.6
3	49.3

Excess Air — Usually about 18 percent but occasionally up to 20 percent

Gas Flow Rate

Unit	lb/hr	cfm (STP)
1	724,760	163,000
2	745,920	168,000
3	1,242,360	280,000

WEYMOUTH*

Stack Height — 266 ft elevation, 231 ft above grade

Stack Inside Diameters— Bottom 15 ft (top of roof of building)
Top 13 ft

Fuel Consumption — 100 gal No. 6 oil/min for each 90-MW unit

Excess Air — 18 percent

Gas Flow Rate — 920,000 lb/hr 200,000 cfm (STP)

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*Indicated values apply to a single 90-MW unit.

Two Gartrell (Ref. 1) probe assemblies were constructed for measurement of SO_2 and SO_3, and fly ash particulates. The results of exploratory tests were not satisfactory for a number of reasons, e.g., condensation could not be eliminated despite the heating units within the Gartrell probe, and reproducibility was not attained with certain of the analytical methods (See Section III.C).

The following modifications were made in the sample system:

(1) An unheated probe was connected to the sampling train as shown in Figure 2 so that travel distance of gas samples from the duct to the first element in the sampling train was minimized (< 12 inches).

(2) Several analytical techniques were compared for the determination of SO_3 concentrations; barium chloranilate, methyl thymol blue with Technicon AutoAnalyzer, and acid-base titrations. Details and evaluations of these analytical procedures are summarized in Section III.C.

(3) With respect to particulate sampling, the nozzle* and alundum thimble** assembly was connected to a separate stainless steel probe rather than to the Gartrell unit.

Since in both cases the particulates were collected at the probe inlet, the change in external components had no effect on system performance. Note final equipment arrangement in Figure 2.

Present gas and particulate sampling procedures as carried out with the equipment arrangement shown schematically in Figure 2 are summarized below.

(1) Ceramic thimbles for fly ash collection are mounted in thimble holders located immediately behind the probe inlet. Fly ash samples are collected over a 60-minute period at a 2 ft^3/min (STP) flow rate.

(2) The gas sampling train consists of a 2-inch diameter glass filter circle to collect any particulate matter (including absorbed SO_3) and four midget absorbers (bubblers). The first bubbler, which is immersed in an ice bath and contains 15 cubic centimeters of isopropyl alcohol, acts as a heat exchanger for condensing water in the gas stream as well as collecting SO_3. The second bubbler contains 15 cubic centimeters of isopropyl alcohol and functions as a backup for SO_3 collection. The third and fourth bubblers contain 15 cubic centimeters of 1-percent hydrogen peroxide solution for collection of

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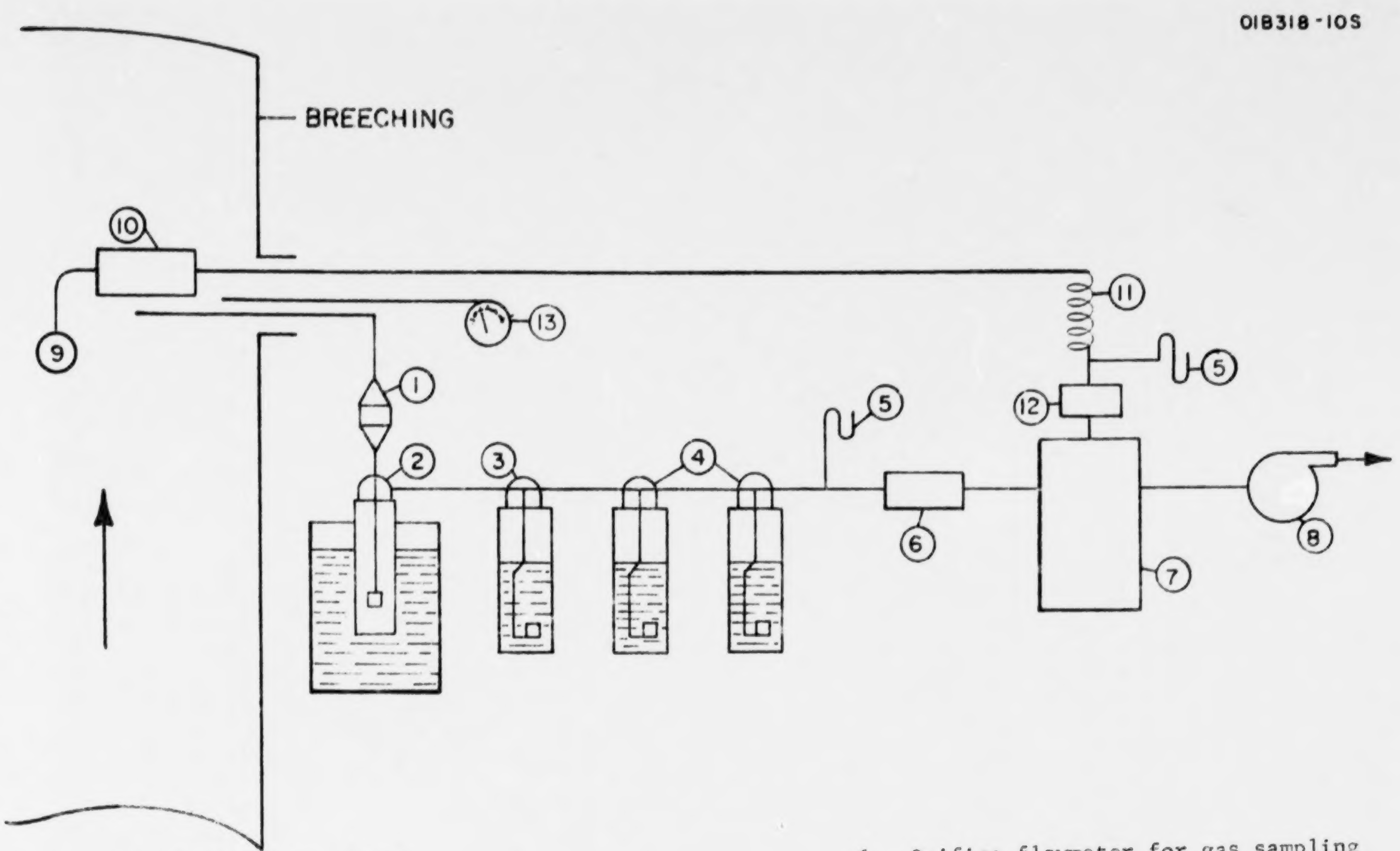
* Western Precipitation Co. Type C1021 thimble holders.

**Coarse porosity, 3.5 cm diameter by 10 cm length, Norton Co., Worcester, Mass. (Size 6406).



1. Particulate filter
2. Standard midget fritted bubbler with 15 cc of 80 percent iso-propanol in ice bath - provides condensate removal and SO_3 collection.
3. Flat midget fritted bubbler 15 cc of 80 percent iso-propanol for SO_3 collection
4. Flat midget fritted bubblers 15 cc 1 percent H_2O_2 for SO_2 collection
5. Static pressure manometer
6. Orifice flowmeter for gas sampling (0.4-0.5 liter per minute)
7. Manifold
8. Sampling pumps
9. Isokinetic probe for particulate sampling
10. Thimble holder
11. Cooling coil
12. Orifice flowmeter for flyash sampling system (40-50 liters per minute)
13. Pyrometer

Figure 2. Stack sampling apparatus.

SO_2. The gas sampling train is operated for 30 minutes at a flow rate of 0.5 liter/min (STP). After each gas sample is collected, air is drawn through the gas sampling train for 30 minutes at 0.5 liter/min to transfer any SO_2 absorbed in the first two bubblers to the third and fourth peroxide bubblers.

During the stack sampling process, two tracer materials were introduced at the base of the stacks, one to permit airborne tracking of the plume and the other to aid in defining the SO_2 loss mechanisms (meteorological and/or chemical) within the plume. The location of the downwind plume was determined from particulate phosphor tracer (FP) blown into a single breeching at a rate of 30 lb/hr. Since FP was used only for tracking purposes, any inequalities in plume concentration resulting from unequal stack dosage or imperfect mixing in the plume was considered unimportant. Mechanisms of sulfur dioxide loss in the atmosphere were defined by releasing 100 cm^3/min of inert sulfur hexafluoride gas (SF_6) into each stack from a lecture bottle through a small rotameter. Simultaneous plume samples of FP, SO_2 and SF_6 were obtained downwind with an instrumented aircraft.

C. CHEMICAL ANALYSES

The analytical procedures used for both stack and aircraft field sampling programs are summarized briefly since their application is well documented in the literature. Several methods were explored during the first part of the program to determine which ones were best suited for the present measurements.

(1) SO_2- West-Gaeke Method. Sulfur dioxide samples obtained from the airborne impinger sampling system were analyzed by the Scaringelli (Ref. 2) modification of the West-Gaeke method adapted for use on a Technicon AutoAnalyzer (method B).

(2) SO_2 - Hydrogen Peroxide Method. Some source samples were analyzed by the H_2O_2 - titration method described by Hochheiser (Ref. 3).

(3) SO_3 - Methyl-thymol-blue Method. Both plume filter samples and source bubbler samples were analyzed initially by the MTB procedure given by Lagrus (Ref. 4). Although preliminary results appeared satisfactory, the MTB method later proved to be unpredictable. Therefore, use of this method was discontinued in favor of the barium chloranilate method below.

(4) Barium Chloranilate Method. The barium chloranilate method (Ref. 5), which has been used for the majority of source tests, applies equally well for SO_2 and SO_3 analyses.

(5) Oxides of Nitrogen - Saltzman Method. Since it is proposed to sample for NO and NO_2, the procedure given by Saltzman (Ref. 6) has been adopted.

(6) Sulfur Hexafluoride - Clemons Method. The procedure of Clemons, et al., (Ref. 7) was selected for SF_6 analyses. The sensitivity of this method and application of SF_6 as a meteorological tracer have been discussed recently by Turk, et al. (Ref. 8). Although contamination problems were experienced in early trials, the exclusion of all laboratory air from sampling loops and chromatographic columns has led to satisfactory results.

D. RESULTS

The results of stack sampling measurements performed at the Salem harbor Station over the period November 17, 1968 through March 27, 1969 are summarized in Tables 3 through 6. Data presented in Table 3 represent exploratory measurements involving the field evaluation of new equipment and experimental techniques. Since many SO_2 samples were stockpiled to reduce the time requirement for chemical analyses (particularly those performed with the Technicon AutoAnalyzer), inconsistencies in SO_x concentration levels were not immediately apparent. It was determined that excessive condensation within the sampling probe and connecting lines led to high SO_2 losses (and conversion to SO_3) prior to entering the gas sampling train, Tests S-1-B through S-5-B, Table 3. Relocation of probe heating coils and temperature sensors led to some improvement but did not eliminate condensation. Although total SO_2 concentration were reasonable with respect to plant heating rates and fuel assay (Tests S-6-A to S-7-A, Table 3), approximately equal SO_2 recoveries in the series-connected bubblers pointed out the need for an increase in H_2O_2 concentration. The recoveries of SO_3 as sulfate from filter washings and isopropanol were also lower than expected.

Tests reported in Table 4 were performed with the sampling assembly shown in Figure 2 in which a short, < 12-inch, connection was made between the probe within the hot duct and the filter inlet. Hydrogen peroxide strength in the SO_2 bubblers was also increased to 1 percent. The results of the above modification led to observed SO_2 concentrations which appeared to agree with those predicted by fuel assay, i.e., seven out of eleven values shown for SO_2 range between 904 and 1064 ppm. Low values noted for Tests 14-B, 15-B, 16-B, and 17-B were the result of leaks and flow meter malfunction in one sampling assembly. Since gas flows were identical in breechings 1 and 2, there is no reason to expect any significant differences in gas composition. This premise is substantiated by the fact that paired particulate fly ash loadings for breechings 1 and 2 show good agreement.

A summary of SO_2 and SO_3 findings is presented in Table 5 for those data considered dependable. Generally, agreement appears satisfactory with respect to calculated values for SO_2 concentrations based on the Salem Harbor Station statistics for coal analysis, Table 7, and gas flow rate, (Table 2). In calculating theoretical SO_2 emissions, it is assumed that 90 percent of the sulfur content of the coal was discharged as sulfur oxides.

TABLE 3

STACK SAMPLES* FROM SALEM HARBOR STATION

Date 1967	Test No.	Unit No.	Breeching	SO_2-ppm			SO_3-ppm			
				1	2	Total	Bubbler		Filter	Total
							1	2		
11/17	S-1-B	3	1	138		138	0.42	0.57	1.3	2.29
	S-2-B	3	1	27		27	0.39	0.18	0.38	0.45
11/21	S-3-A	3	2	0		0	0.29	0.36	1.23	1.88
	S-3-B	3	1	235		235	0.21	0.35	1.27	1.83
11/28	S-4-A	3	2	13.7		13.7	0.17	0.71	1.66	2.54
	S-4-B	3	1	242		242	0.097	0.37	1.05	1.52
	S-5-A	2	1	254		254	0.18	0.26	1.49	1.93
	S-5-B	2	2	245		245	0.65	2.76	1.24	4.67
12/5	S-6-A	2	1	428	390	818	1.8	1.3	1.88	4.98
	S-6-B	2	2	387	297	684	0.28	0.37	1.61	2.27
	S-7-A	1	2	430	424	854	0.11	0.11	1.63	1.85
	S-7-B	1	1	224	0	224	0.64	0.17	1.03	1.84

*Using 12-foot heated Gartrell probe.

TABLE 4

STACK SAMPLE DATA FOR SALEM HARBOR STATION, UNIT NO. 1[a]

Date/No. 1968	Breech No.	SO_2-ppm			Filter	Wash	SO_3-ppm			Flyash (mg/m^3)
		1	2	Total			1	2	Total	
March 7										
S-12-A	1	---	--	----	----	----	----	----	---	175
12-B	2	977	0	977	----	----	----	----	---	400
13-A	1	990	0	990	----	----	----	----	---	359
13-B	2	1008	0	1008	----	----	----	----	---	360
March 15										
S-14-A	1	904	0	904	1.0[b]	3.8[c]	2.0	3.6	10.6	1030
14-B	2	346	48	394	1.2[b]	2.5[c]	3.54	2.57	9.8	1270
15-A	1	980	0	980	----	3.3[c]	0.61	0.55	---	458
15-B	2	493	0	493	3.5[b]	1.3[c]	3.01	1.23	9.0	885
March 22										
S-16-A	1	1061	0	1061	0	0.3	3.15	2.78	6.2	465
16-B	2	326	46	372	----	0	0	0.72	---	461
17-A	1	1045	0	1045	3.15	0.4	1.57	1.37	6.5	1285
17-B	2	416	0	416	----	0	0	0		1054

[a] SO_2 and SO_3 analyses by Barium Chloranilate, except as shown.

[b] Acid titration analyses.

[c] Methyl thymol blue and Technicon Autoanalyzer.

TABLE 5

SO_x SUMMARY

Date 1968	SO_2, Observed, ppm			SO_3, Observed, ppm			SO_2 Calc., ppm	S in Coal, (percent) Dry Basis
	No. Tests	Mean Value	Avg. Dev.	No. Tests	Mean Value	Avg. Dev.		
3/7	3	992	11	--	---	---	1100	1.79
3/15	2	942	38	3	9.8	0.5	1310	2.0
3/22	2	1053	8	2	6.4	0.2	1330	2.19

TABLE 6

FLYASH SUMMARY*

Date 1968	Test No.	Flyash (mg/m^3)	Avg. Dev.	Average Unit Output, MW	Ash in Coal, (Percent) Dry Basis
3/17	13	300	1	87	7.17
3/15	14	1150	120	86	6.91
	15	672	214		
3/22	16	463	2	71	8.15
	17	1170	115		

*The "average" value of the flyash loading calculated from the above five values is 751 mg/m^3 ($0.33 gr/ft^3$) with an average deviation of 342 mg/m^3. This gross average is, however, not significant in terms of average plant output/day until weighting factors are established.

TABLE 7

COAL ANALYSIS FOR SALEM HARBOR STATION

AS RECEIVED

Week	Water	Volatiles	Ash	Fixed Carbon	BTU/lb
3/3 - 3/10	4.52%	37.99%	6.85%	50.64%	13,420
3/10 - 3/17	4.43%	38.72%	6.61%	50.24%	13,470
3/17 - 3/24	5.88%	37.65%	7.67%	48.80%	13,210

MOISTURE FREE

Week	Volatiles	Ash	Fixed Carbon	Sulfur	BTU/lb
3/3 - 3/10	39.79%	7.17%	53.04%	1.79%	14,050
3/10 - 3/17	40.52%	6.91%	52.57%	2.0%	14,090
3/17 - 3/24	40.00%	8.15%	51.85%	2.19%	14,030

The summary of fly ash concentrations given in Table 6 includes all measurements cited in Table 4 since there was no apparent malfunction in the sampling systems. The observed loading variations can be reasonably associated with intermittent reentrainment of particulates from electrostatic precipitator electrodes and duct surfaces. In addition, it was expected that the fluctuations in ash content (as well as sulfur) would vary to a greater degree than shown in Tables 6 and 7 if assays were performed on an hourly rather than a weekly basis. The overall average fly ash concentration of the stack effluent, 751 milligrains/m^3 (or 0.33 grains/ft^3) was within the expected range based upon the ash content of the coal and a nominal 80 to 90 percent efficiency for electrostatic precipitators.

E. DISCUSSION

Stack sampling measurements presented in this section indicate that the concentrations of SO_2 and SO_3 discharged from the Salem Harbor stacks during the testing period were approximately 1000 and 9 ppm, respectively. Particulate fly ash concentrations measured downstream of the electrostatic precipitators averaged 0.3 grains/ft^3 (750 milligrains/m^3). Based upon fuel assays and combustion parameters, the above field measurements appear consistent with expected performance.

IV. FIELD STUDIES - AIRCRAFT SAMPLING

A. INTRODUCTION

The objective of the aircraft plume sampling program is to determine the extent of SO_2 loss in the atmosphere as a consequence of chemical reactions related to environmental and plant operating variables. A major task of the plume sampling program is to measure the downwind concentrations of sulfur oxides and conservative SF_6 tracer in plumes from large fossil-fueled combustion sources. Technical requirements for this task include:

(1) Single sources of sulfur oxides whose plumes can be traced individually over extended distances, approximately 25 miles, and for periods up to two hours.

(2) Measurement of source parameters, e.g., stack gas composition, temperature and mass release rate at cooperating power stations, Section III.

(3) Measurement of meteorological parameters to determine the approximate direction and shape of the plume, Section VIII.

(4) Prediction of approximate downwind axial concentrations of plume components during the actual plume tracking period based upon concurrent measurements of meteorological and source parameters, Section VIII.

(5) Measurement of such environmental factors as solar flux, humidity, temperature, and other plume constituents bearing upon the atmospheric chemistry of sulfur compounds.

(6) Development of aircraft-borne sampling techniques which will permit representative measurements of SO_x concentrations within selected portions of the plume.

(7) Development of a technique for rapidly locating plume boundaries which cannot be detected visually beyond one or two miles from the source.

Theoretically, the above criteria should allow comparison of actual and predicted SO_2 concentrations at various downwind distances from which the magnitude of chemical loss rates might be inferred. In practice however, the predictive capability of meteorological diffusion models lacks the precision and accuracy needed for such comparisons. To circumvent this problem, it is essential to introduce metered amounts of a tracer material which is mixed completely within the stack and remains with, but does not react with, plume constituents. Since the selected tracer, SF_6, and SO_2 (or other gaseous compounds of interest) are subject to identical meteorological dilution phenomena, establishment of downwind concentration ratios for SO_2 and SF_6 provides a direct measure of SO_2 reaction rate in the atmosphere.

Three techniques were investigated for locating the plume, (a) measurement of space charge produced by charging of plume constituents during the combustion or precipitation process, (b) sampling for solid fluorescent pigments which were injected into the base of the stack,and (c) measurement of SO_2 concentrations with an automatic analyzer having rapid time response. Detection of plume boundaries by space charge and FP particle measurements was limited to less than two miles. A Sign-X electroconductivity analyzer proved a satisfactory device for extended plume tracking (at least 12 miles) and, with correction for ambient CO_2 levels, also provided reasonable estimates of SO_2 plume concentrations. Two dimensional mapping of plume boundaries was accomplished for the effluents from the Salem Harbor and Edgar Station plumes for selected crosswind traverses. Average SO_2 concentrations were determined at these locations by integration of Sign-X recorder readings.

Measurements of SO_3 concentrations were also made in the Edgar plume with a sampling train consisting of an all-glass filter for particulate $SO_4^=$ and a midget impinger for SO_2 collection (West-Gaeke method).

B. EXPERIMENTAL EQUIPMENT

Instrumentation required for environmental measurements and plume tracking includes:

(1) Air temperature, wet and dry bulb.

(2) Liquid water content (Johnson and Williams hot-wire instrument).

(3) Air speed, altitude, heading.

(4) Time and event.

(5) Solar radiation.

(6) Sign-X electroconductivity SO_2 analyzer for plume detection and SO_x concentration determination.

The information from these instruments is recorded continuously or noted periodically in the flight log.

Air sampling equipment includes:

(1) Three-liter Saran bag sample collectors for fluorinated tracer, SO_2 and NO_x.

(2) Midget impingers and filters for SO_2 and SO_3 collection.

(3) Membrane filters for fly ash.

Details on instrument selection, calibration, and measurement procedures are given in Appendix A.

C. ANALYSES

Analyses of samples obtained during flights through stack plumes have been discussed previously in Section III.C.

D. RESULTS

A summary of all aircraft operations during the first year of the program, Table 8, indicates the purpose of each flight and the type of experimental measurements performed. Several of the early flights were intended to study and develop instrument systems essential to the plume measurements program. Good stagnation conditions were not realized during much of the fall of 1967 such that the use of FP tracer (zinc cadmium sulfide) and the measurement of atmospheric space charge did not provide capability to track the plume beyond two miles. Instrument malfunction also contributed to the unsatisfactory performance of the FP monitor (Ref. 9) which in theory should detect concentrations as low as 1 particle/cm^3. Although the Singco field mill could detect qualitatively voltage gradients as low as 20 V/cm, this was not sufficient to measure the space charge produced by charged particles exiting from the Salem Harbor stack. Operational details of the field mill are given in Appendix A. Subsequent adoption of a Sign-X electroconductivity analyzer proved a successful means not only for delineating plume boundaries but also for establishing estimates of axial concentration, tests of January 12, 19, 20, Table 8.

Three flights were performed during the early part of the program year in which attempts to measure FP were made to define plume boundaries (November 3, 9, and 21, 1967). The first two flights were conducted over Boston Edison's Edgar Station at Weymouth (oil fired) and the third over New England Electric System's Salem Harbor Station (coal fired). A primary goal of all three flights was the evaluation and improvement of plume tracking techniques and assessment of other sampling instrument performance. Direct radio communication between the aircraft and ground crew was maintained throughout the test period. As a result of instrument malfunction, FP was not detected during the first flight (November 3, 1967) but SO_2 impinger samples and SF_6 bag samples were obtained 1/2 and 3 miles downwind by visual sighting of the plume.

Meteorological soundings were conducted before and after the November 9, 1967 flight. FP detection in the plume was successfully accomplished at 1 mile, but instrumental difficulties prevented further down-range tracking. Sulfur dioxide impinger samples and SF_6 bag samples were obtained at 1,3, and 7-mile ranges, although visual tracking was not precise.

TABLE 8

SUMMARY OF AIRCRAFT SAMPLING FLIGHTS THROUGH PLUMES

Date	Power Station	Purpose	Data Acquired
3 Nov 67	Edgar Station, Weymouth	Radio communication check. FP check.	No FP data, instrument malfunction. SF_6 and SO_2 impinger samples taken at 1/2 and 3 miles, visually. No meteorological measurements.
9 Nov 67	Edgar Station, Weymouth	FP check.	Meteorological soundings before and after plume tracking. SO_2 and SF_6 samples taken at 1, 3 and 6 miles, visually.
21 Nov 67	Salem Harbor	FP check.	Meteorological soundings and wind star taken. Some FP indications of plume location.
5 Dec 67	Salem Harbor	Field Mill check.	Tracked plume with Field Mill out to 3 miles.
6 Dec 67	Salem Harbor	Field Mill and FP indicator trails.	Meteorological soundings before and after Field Mill and FP measurements. SF_6 and SO_2 samples taken over stack at various altitudes.
7 Dec 67	Salem Harbor	Field Mill and FP indicator trails.	Meteorological soundings. Field Mill data taken. FP instrument malfunction.
20 Dec 67	Salem Harbor	FP check.	Meteorological soundings taken. No FP indication obtained.
12 Jan 68	Salem Harbor	Sign-X analyzer tried in aircraft.	Good and useful indications out to approximately 6 miles.
19 Jan 68	Edgar Station Weymouth	Sign-X SO_2 analyzer check.	Meteorological soundings taken. SO_2 tracking of plume and SO_2 concentrations mapped out to 12 miles.
20 Jan 68	Salem Harbor	Sign-X SO_2 analyzer check.	Meteorological soundings taken. Plume tracking and SO_2 mapping obtained out to 7.1 miles.

The November 21 flight was performed at Salem Harbor, and meteorological soundings and wind star flight patterns were flown before and after plume sampling. Although the FP monitor performed reliably throughout the flight, only marginal indications of plume dimensions were obtained, partly as a consequence of the unfavorable turbulent wind pattern. Relatively few plume samples were obtained since visual sighting was not possible.

Available plume data for this period is summarized in Table 9. The SO_2 values appear reasonable but should only be accepted as rough estimates since plume boundaries were poorly defined. High values for SO_3 are suspect and probably result from an unavoidable delay in sample analysis.

TABLE 9

SUMMARY OF SULFUR OXIDE CONCENTRATIONS IN EDGAR STATION STACK PLUMES

Date	Flight Number	Distance (miles)	SO_2[a] ppm	SO_3[b] ppm
3 Nov 67	FW-1	3	0.14	0.72
9 Nov 67	FW-2	1	0.17	0.72
		3	0.14	0.18
		7	0.085	0.12

[a] West-Gaeke Analysis

[b] Titration of filter washings.

Chromatographic analyses of SF_6 samples were conducted by both direct and preconcentration techniques and calibration curves were established. Analysis of plume samples yielded unreasonably large values which were later shown to be the result of sample contamination.

Four additional flights were conducted to evaluate feasibility of the field mill measurement of plume edges (December 5, 6, 7, and 20, 1967). Plume indications were obtained with both instruments only at relatively short distances from the stack top. Maximum fields of 140 V/cm were recorded at Salem but tracking could not be carried beyond 2 miles. The FP monitor proved to be only marginally better.

As a result of this performance, a Sign-X electroconductivity analyzer* with a nominal 8-second time constant was installed in the aircraft. A more recent model with a 2.5-second response time was not available for use on the program at that time.

Two flights were conducted (January 19 and 20) in which excellent plume tracking results were obtained using the above Sign-X analyzer. The first flight was made from the Edgar Station at Weymouth during the early afternoon. Approximate plume boundaries found at four locations are shown in Figure 3. At least four passes were made at each location at four altitudes. The apparent plume boundaries, as a function of altitude, are plotted in Figure 4. Note that widths and not locations in space are plotted in this figure since the plume traverses are arbitrarily centered and not spatially registered. In Figures 3 and 4 the boundaries represent minimum responses, i.e., nominally 0.01 ppm SO_2. The apparent peak SO_2 concentrations observed are given in Table 10. It may be seen that only at the shortest distance is any noticeable concentration gradient observed although the precision of the measurements is fairly good. Since the plume widths are at least two time constants wide, the absolute value of the peak SO_2 concentration is underestimated by a factor of no more than two for any reasonable distribution.

TABLE 10

OBSERVED SO_2 CONCENTRATIONS

Flight of 1/19/68

Range (miles)	Altitude (feet)	Peak Concentration[†] (ppm)
1.75	500	0.29
	700	0.25
	900	0.18
	1100	0.15
4.5	500-1000	0.16 ± 0.02
7.5	500-1000	0.11 ± 0.01
12	800-1400	0.11 ± 0.005

[†] Sulfur dioxide concentrations corrected for CO_2 background. It is assumed that the remaining conductivity is due to SO_2.

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*Sign-X, Inc., Essex, Connecticut.

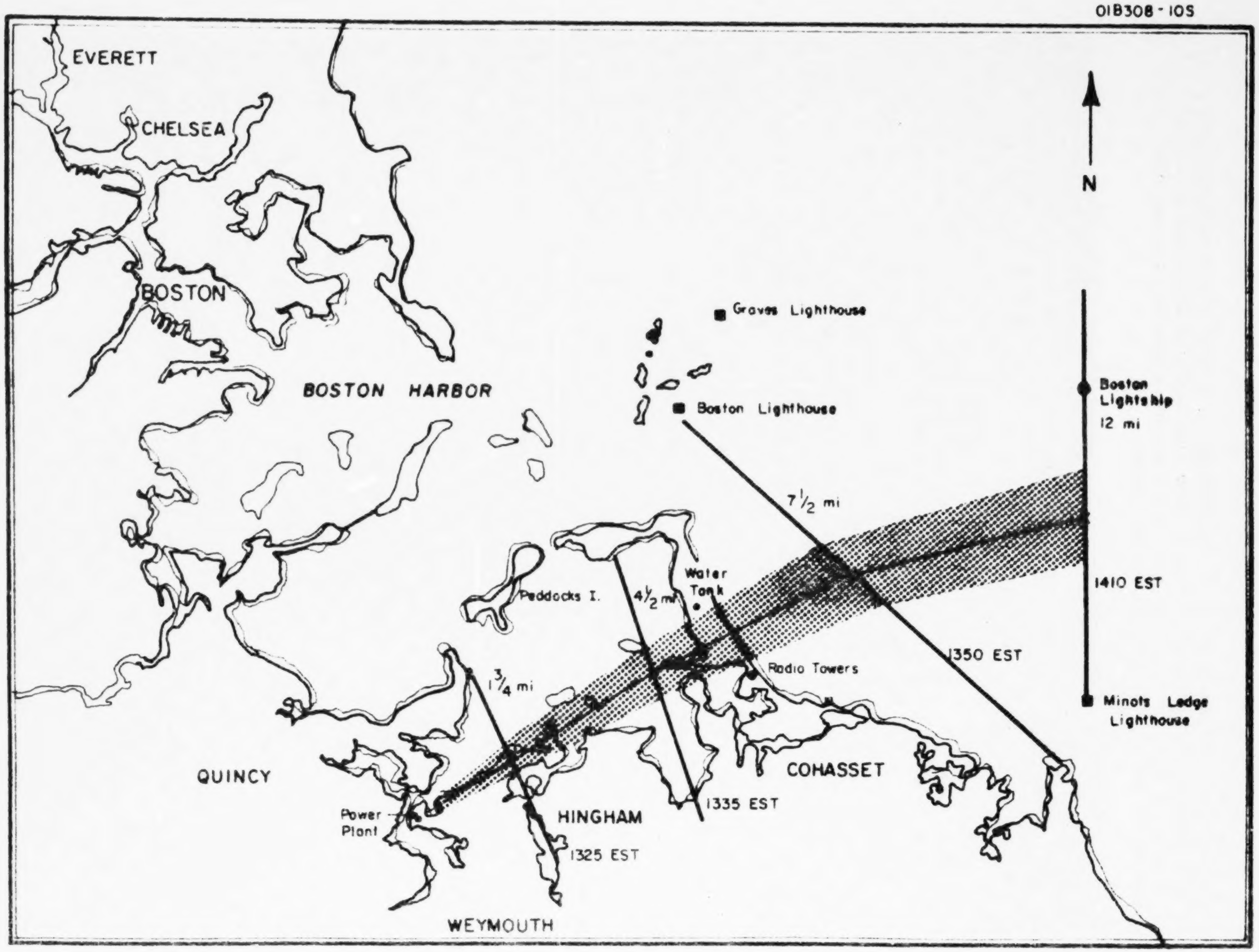
01B308-10S
N
EVERETT
CHELSEA
BOSTON
BOSTON HARBOR
Graves Lighthouse
Boston Lighthouse
Boston Lightship
12 mi
7 1/2 mi
1410 EST
1350 EST
Minots Ledge Lighthouse
Peddocks I.
4 1/2 mi
Water Tank
Radio Towers
1 3/4 mi
QUINCY
COHASSET
1335 EST
Power Plant
HINGHAM
1325 EST
WEYMOUTH

Figure 3. Plume map of January 19, 1968 at Edgar station.

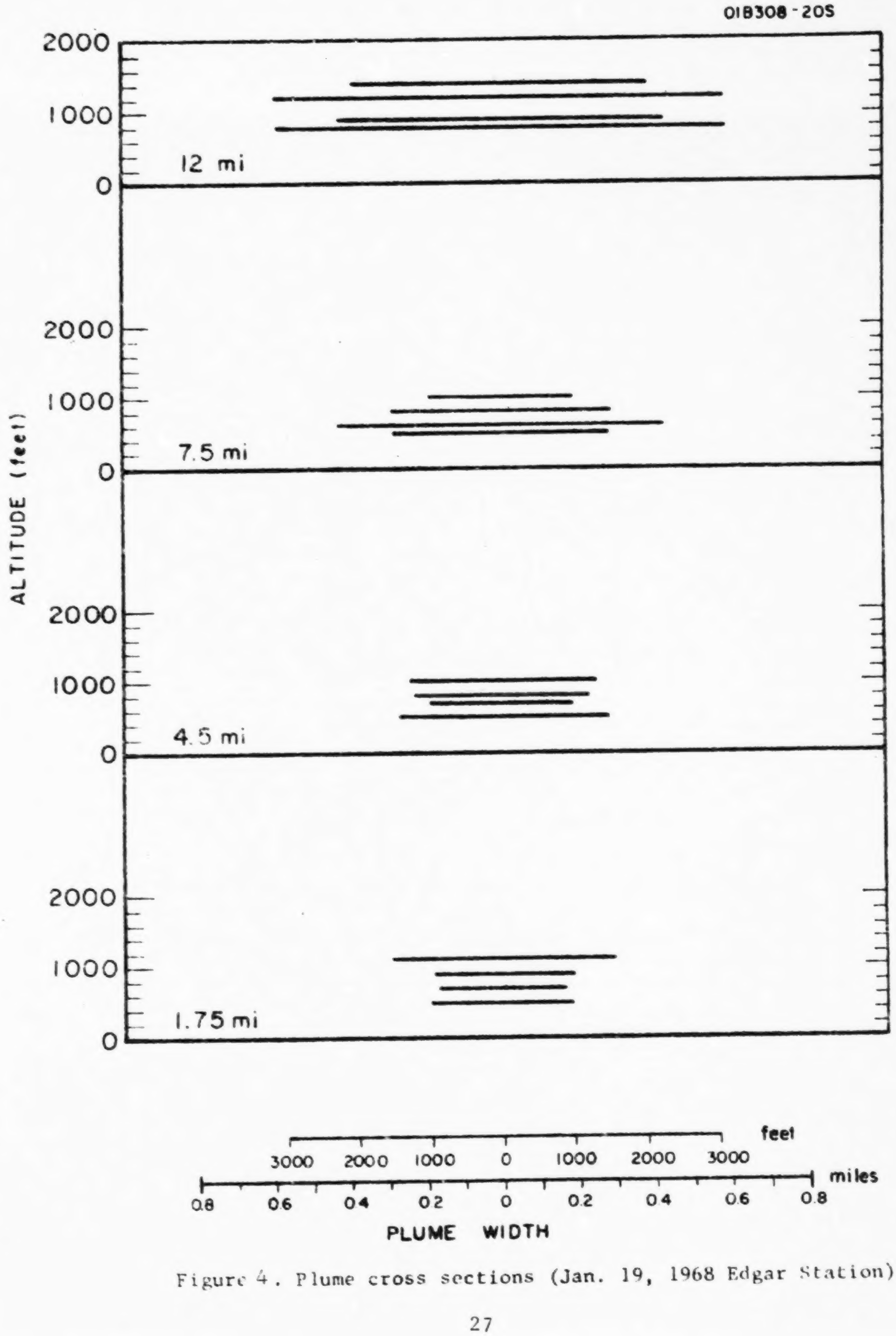

Figure 4. Plume cross sections (Jan. 19, 1968 Edgar Station).

Following the successful test of the SO_2 electroconductivity analyzer on January 19, 1968 at Edgar Station, a more detailed test was conducted at Salem Harbor on January 20 in order to assess plume tracking for the low visibility plume at this coal-fired station.

Measurements were made early in the afternoon. Average wind speed computed from aircraft parameters was 15 mph. The air temperature profile at 1315 EST revealed a lapse rate of approximately 0.3°C per 100 feet (from 5.8°C at 500 feet to 2.9°C at 1500 feet) or near-neutral atmospheric stability.

Location of certain plume edges were mapped by stopwatch measurement of travel time at known heading, altitude and speed from a known location, to the moment at which Sign-X instrument response above background was observed. Since data of apparently good quality were obtained, a fairly detailed analysis has been prepared to improve future field sampling operations and to simulate results obtained with the faster response instrument which has been ordered for this program (2.5-second time constant).

Data from 23 traverses of the plume from the Salem Harbor experiment of January 20, 1968 are shown in Table 11. Owing to the experimental nature of the flight, the traverses were obtained in reverse order, that is, from the plume farthest out, back in toward the source, rather than from the source outward following a given section of the plume. This experimental approach makes it difficult to interpret the results in any consistent fashion, as will be observed during the discussion below, because the continuity of the plume is in doubt.

Data presented in Table 11 include the traverse number (Col. 1), the aircraft sampling altitude in feet (Col. 2), the indicated air speed in miles per hour (90 mph = 132 ft/sec, 80 mph = 117.4 ft/sec) (Col.3), the magnetic heading (Col. 4), and the apparent plume width and peak SO_2 concentration (Cols. 5 and 6) together with remarks pertaining to the traverse location with respect to fixed objects on the surface below the airplane.

Actual records of indicated analyzer conductivity are shown in Figures 5(a) and 5(b) as reproduced on linear coordinate paper from the curvilinear (Esterline-Angus) record taken in the airplane. The shape of the conductivity indication is a function of the shape of the actual SO_2 concentration in the plume and the instrument time response (8 seconds). The characteristics of the analyzer output record in response to a series of assumed input waveforms (square, trapezoid, triangle) are discussed in Appendix B.

Plume widths and maximum SO_2 concentrations recorded in Table 11 (Cols. 5 and 6) are taken from data recorded in Figures 5(a) and 5(b). The recorded plume width in Table 11 is the value of the length of the trace as estimated above background. Maximum SO_2 concentration has been determined from the recorded maximum reading corrected for instrument response at an assumed value of CO_2 of 300 parts per million.

TABLE 11

AIRCRAFT SAMPLES OF SO_2[a] IN STACK PLUME FROM SALEM HARBOR STATION

20 January 1968

Traverse No.	Altitude (ft)	Speed (mph)	Heading	Plume[b] Width (ft)	SO_2 Max.[c] (pphm)	Remarks
Runs over Graves Island and Great Egg Rock, 7-1/2 miles from Salem Harbor						
1	800	90	180	7000	4.2	Over pink house, halfway between Town Head and Eagle Head, Manchester, Mass., 33 seconds.
2	600	90	340	220	2.1	
3	1000	90	180	4400	3.0	No indication.
4	700	90	340	7920	3.2	1 minute, 10 seconds from seaward edge of plume to shore.
5	900	90	S?	4400	5.3	End 1338 EST. End runs over Graves Island and Great Egg Rock.
Runs over west edges of Bakers Island and Great Misery Island (4.1 miles)						
6	900	90	310	2640	2.9	1 minute, 15 seconds to shore from seaward edge, calibrate.
7	800	90	180	3520	4.1	Shoreward edge 50 seconds from shore, 1 minute, 10 seconds from shore, seaward edge.
8	700	80	N	2750	4.0	1 minute from seaward edge to shore.
9	600	80	S?	4700	6.4	

TABLE 11 (continued)

Traverse No.	Altitude (ft)	Speed (mph)	Heading	Plume Width (ft)[b]	SO_2 Max.[c] (pphm)	Remarks
10	500	80	310	5100	5.7	Seaward edge 25 seconds from west tip of Bakers Island.
11	400	80	S	5500	2.8	End 1358 EST. End runs above west edges of Bakers and Great Misery Islands.
Run over Gray's Rock, Coney Island, and Great Haste Island (1.8 miles)						
12	400	80	N	7040	6.7	Seaward edge 15 seconds from foundation on Coney Island.
13	500	80	S?	5500	10.7	Shoreward edge 6-7 seconds south of Great Haste Rock.
14	600	80?	310	7040	13.1	Headings 310 and 150 (above?).
15	700	80?	150?	5500	12.0	
16	800	80?	N	5500	3.2	
17	900	80?	S	4700	10.1	
18	1000	90	N	6520	14.0	Seaward edge 20 seconds north of Coney Island at 90 miles per hour.
19	1100	80	S	6250	13.6	1415 EST end 1100-foot run.
20	1300	80	N	8650	17.6	

TABLE 11 (continued)

Traverse No.	Altitude (ft)	Speed (mph)	Heading	Plume Width (ft)[b]	SO_2 Max.[c] (pphm)	Remarks
21	1500	80	S	9400	11.4	Shore edge 15 seconds south Great Haste Island.
22	1700	80?	N	5500	11.4	
23	1900	80?	S	?	7.9	

[a] Obtained with Sign-X SO_2 continuous analyzer based on conductivity of water.

[b] Apparent plume width from recorder chart, uncorrected for analyzer lag.

[c] Uncorrected for analyzer undershoot.

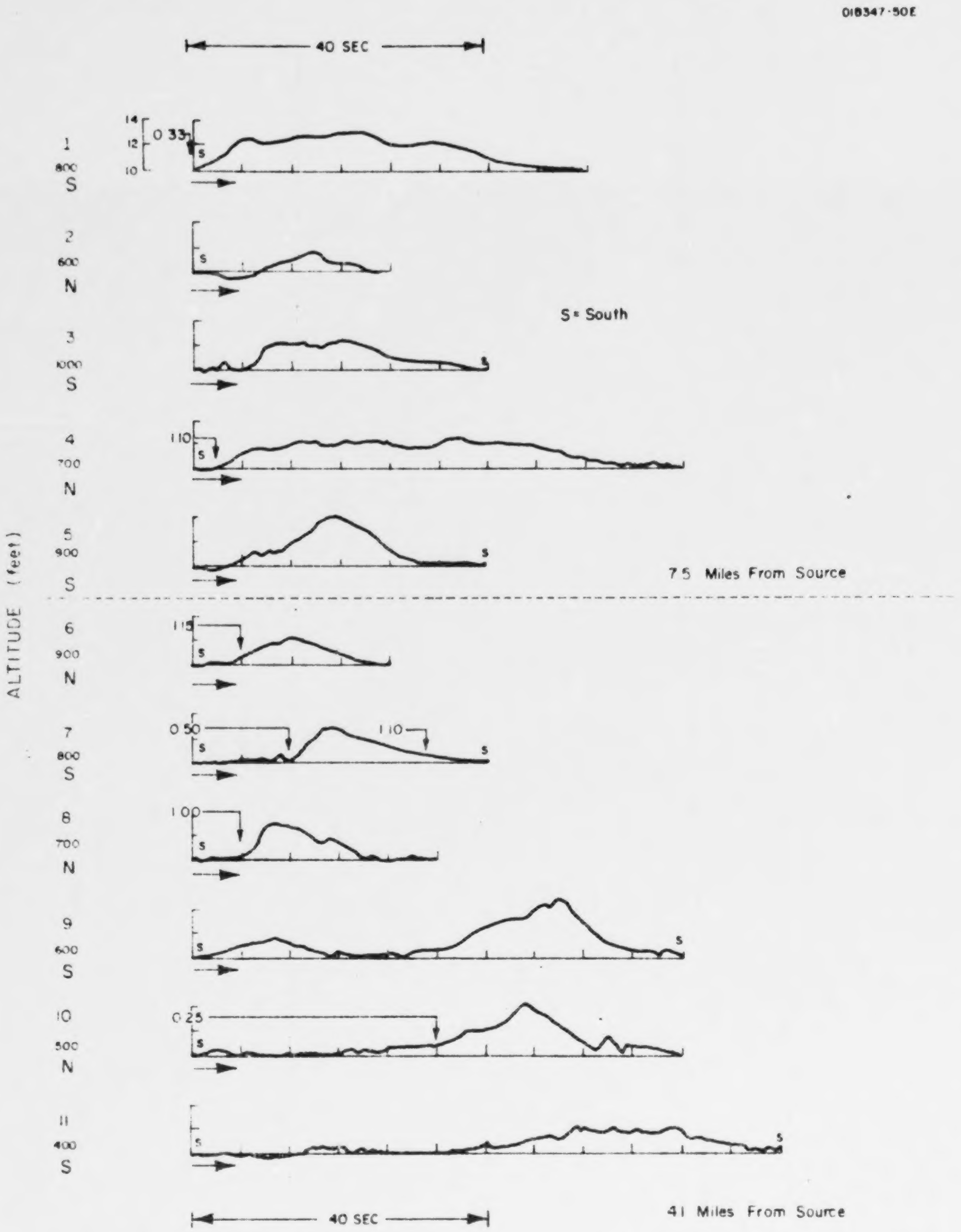

Figure 5(a). Sulfur dioxide concentration in stack plume from Salem Harbor Station, 20 Jan. 1968, at 7.5 and 4.1 miles from source.

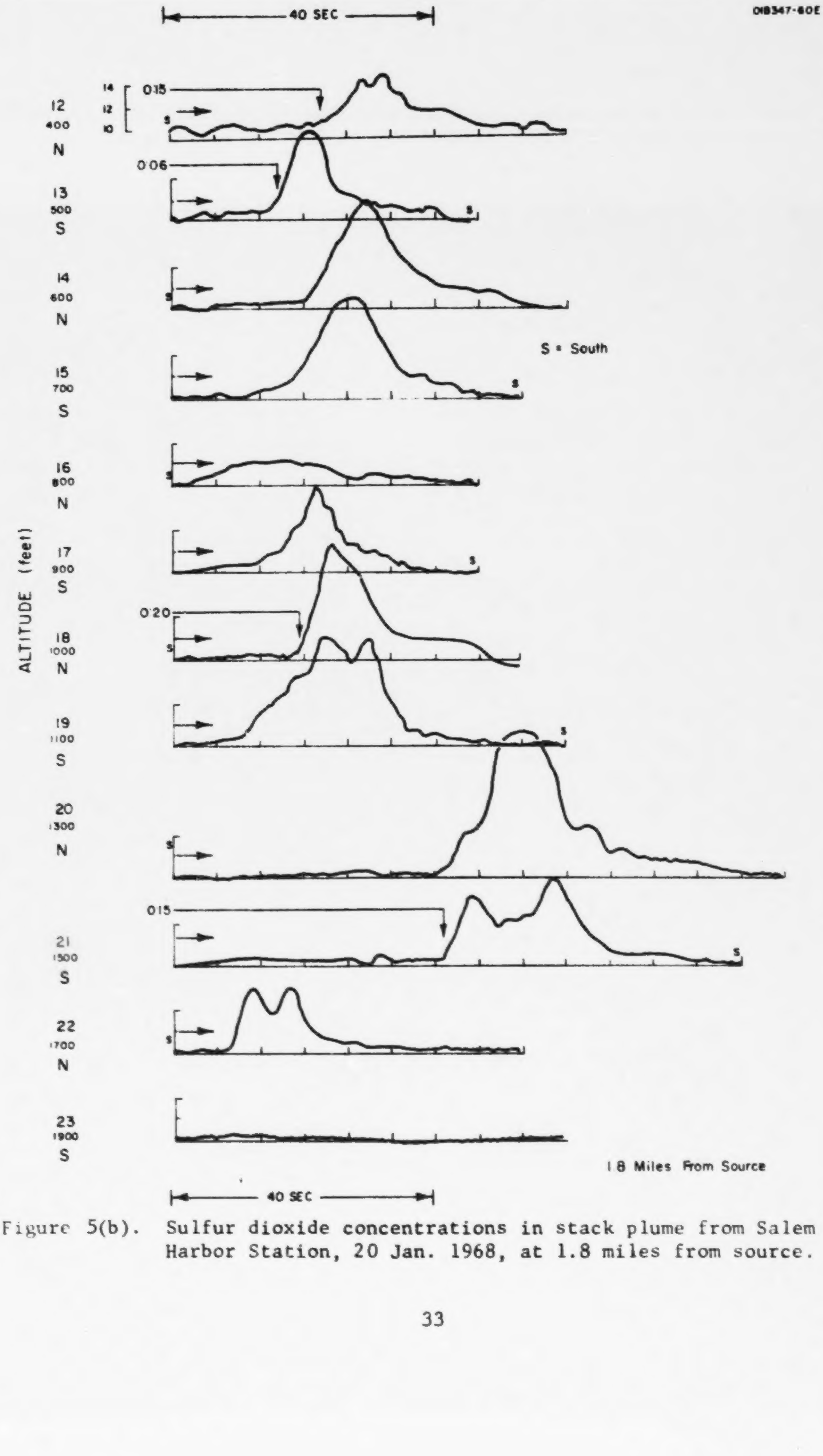

Figure 5(b). Sulfur dioxide concentrations in stack plume from Salem Harbor Station, 20 Jan. 1968, at 1.8 miles from source.

The calibration curves provided with the instrument, plus instrument check in the aircraft, yielded the following calibration:

$$x, \text{ ppm } SO_2 = \frac{y(\%\text{ F.S. Recorder Value})-10}{75}$$

at 300 parts per million CO_2. The reduction of data from the Sign-X analyzer requires a knowledge of the CO_2 background, since CO_2 and SO_2 are recorded simultaneously. This estimation of CO_2 was not made during these preliminary flights.

The approximate spatial location of the plume is illustrated in Figure 6 as deduced from the recorded flight data and observer notations presented in Table 11. Since these traverses were taken backwards, i.e., flying upwind toward the stack rather than downwind in a single parcel of plume as it moved away from the stack, no reasonable deductions can be made regarding the shape of the consecutive profiles. It does appear, however, that a higher layer may have been separated from the plume and not observed at the 4.1 and 7.1-mile traverses. Measurements should not be terminated when a single higher altitude traverse indicates no response. If the aircraft is available, higher altitude traverses should be attempted.

The correction of the apparent plume width is a function of the input SO_2 pulse shape, as discussed in Appendix B. An attempt was made to interpret the analyzer decay characteristic in terms of the half concentration of the last peak from the data given in Figures 5(a) and 5(b). This discussion is included as Appendix C. Peak concentration recorded is also a function of input SO_2 pulse shape, and from the observed shapes it can be concluded tentatively that the values of maximum SO_2 concentration may be low in many cases by a factor of as much as two.

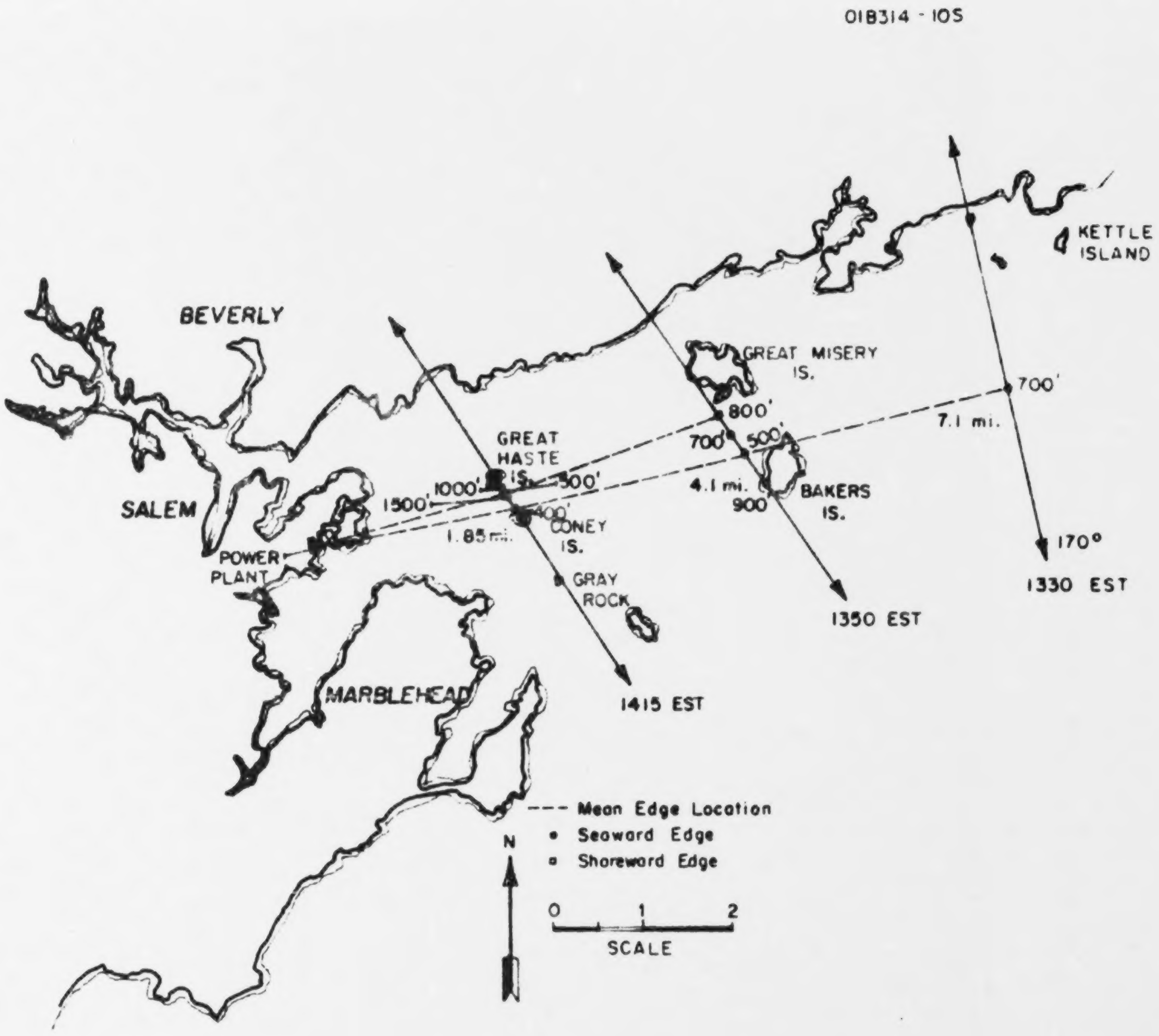
018314 - 105
BEVERLY
SALEM
POWER PLANT
MARBLEHEAD
GREAT HASTE IS.
CONEY IS.
GRAY ROCK
GREAT MISERY IS.
BAKERS IS.
KETTLE ISLAND
1500'
1000'
300'
400'
1.85 mi.
800'
700'
500'
900
4.1 mi.
700'
7.1 mi.
170°
1330 EST
1350 EST
1415 EST
--- Mean Edge Location
• Seaward Edge
▫ Shoreward Edge
N
0
1
2
SCALE

Figure 6. Approximate location of plume edges at Salem as function of aircraft altitude and distance, 20 January 1968.

V. LABORATORY STUDIES - PILOT PLANT FACILITY

A. INTRODUCTION

The field test program described in Sections III and IV is intended to determine the behavior of sulfur oxides in stack plumes under a variety of operational and environmental conditions. The laboratory studies described in this section are designed to investigate under controlled conditions the phenomena observed in the field. Thus an important component in the laboratory installation is a pilot plant combustion system with which real flue gas effluents can be generated for subsequent studies under simulated field environmental conditions.

During this period, a pilot plant flue gas generating facility was designed by the Riley Stoker Corporation of Worcester, Massachusetts, under a cooperative cost-sharing and user agreement with GCA Technology Division. The pilot plant has been constructed under Riley's direction at GCA's Bedford laboratory. Following steady-state combustion tests[*] with oil and coal firing, the unit has been accepted as operational.

B. DESCRIPTION

The model for the design of this equipment was the combustion plant for pulverized coal (25,000 to 50,000 BTU per hour) operated successfully by the U. S. Bureau of Mines. The GCA-Riley system, however, is also equipped to burn No. 6 residual oil at the same heating level, 50,000 BTU per hour. To our knowledge, the successful firing of heavy oils at such low heating rates has not been performed in this country. Provision is also made for propane gas firing so that furnace interior surfaces can be brought up to temperature prior to switching to oil or coal. Fuel composition including sulfur content, combustion temperatures, air reheater exit temperatures, air-to-fuel ratios, and gas cleaning equipment are subject to controls in order to provide pilot plant effluents which are typical of those from similar field combustion processes. Operational details and an isometric drawing indicating all components of the pilot plant are shown in Appendix D.

C. RESULTS

Initial operation of the pilot plant was carried out with the combination propane-heavy oil burner head shown in the upper right corner of Figure D-1, Appendix D. The decision to fire residual oil before pulverized coal was based upon the fact that heavy oil firing at low rates of the order of 50,000 BTU per hour had not been attempted in this country. Therefore, it was desirable to determine if any major unexpected problems existed.

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[*] Coal firing tests completed during second year program.

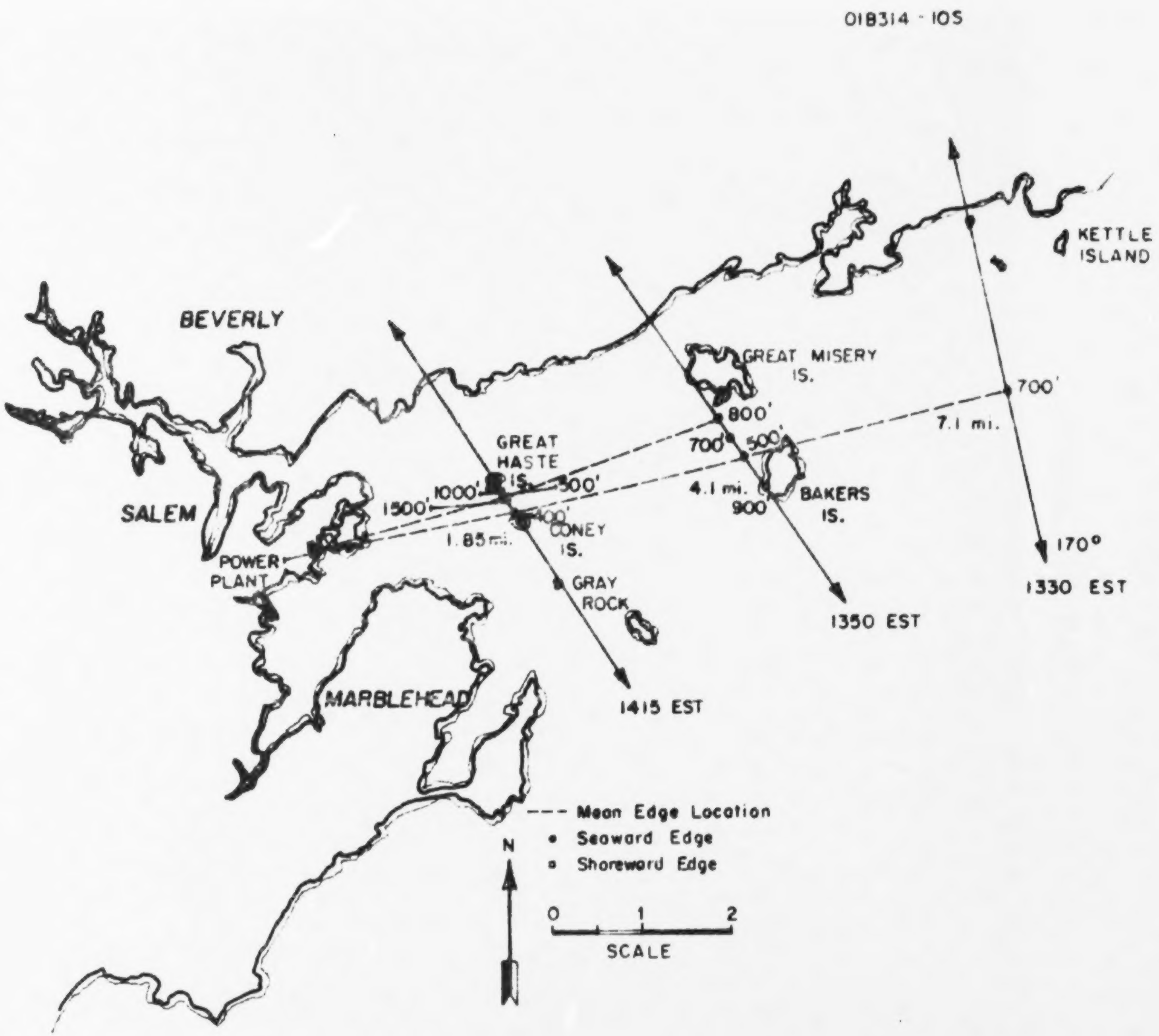
018314 - 105
BEVERLY
SALEM
POWER PLANT
MARBLEHEAD
GREAT HASTE IS.
CONEY IS.
GRAY ROCK
GREAT MISERY IS.
BAKERS IS.
KETTLE ISLAND
1500'
1000'
300'
400'
1.85 mi.
800'
700'
500'
900
4.1 mi.
700'
7.1 mi.
170°
1415 EST
1350 EST
1330 EST
--- Mean Edge Location
• Seaward Edge
▫ Shoreward Edge
N
0
1
2
SCALE

Figure 6. Approximate location of plume edges at Salem as function of aircraft altitude and distance, 20 January 1968.

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---

*Coal firing tests completed during second year program.

During February 1968, preliminary operating tests and checkout of all components were begun for the pilot plant combustion system. Following an extended refractory drying period (100°F per hour) at low heat input with propane (25,000 BTU per hour), the furnace brick temperature was brought up to 1900°F for No. 6 oil firing.

During this first period of oil firing, the following observations were made:

(1) Furnace temperature must be brought to approximately 1900°F before stable oil fires without sparklers can be established. The operating temperature of the brick when firing oil is between 2000°F and 2100°F. These temperatures are measured at a point 2 inches inside the face of the brick.

(2) The flue gas temperature may be controlled at the desired value (about 300°F) by varying the flow of air to the air heater, which is in effect a flue gas cooler.

(3) It is possible to maintain good fires and pilot plant performance with heavy oil firing rates from 40,000 BTU per hour to 75,000 BTU per hour.

(4) Stable fires and good pilot plant performance can be obtained with excess air varying from 0, or stoichiometric, to 30 to 40 percent. Smoke does not appear from the stack until the combustion air drops below stoichiometric.

(5) Fuel oil temperature was not a critical factor in burner performance. If the fuel oil temperature was below 200°F, an unstable fire would result and there would be sparklers present. From 200°F to 240°F, the combustion conditions were excellent and little change could be noted with varying oil temperature within this range. An oil supply pressure of 6.3 psig resulted in the best firing conditions.

(6) Furnace draft is a critical factor in determining oil burner performance. Optimum furnace draft was established at 0.4 inches of water negative.

Following shutdown of the furnace, inspection of refractory linings showed no signs of soot and carbon deposits. However, gummy deposits on the propane burner required recleaning before satisfactory re-ignition could be accomplished. It appears that this problem was the result of momentary excursions into positive furnace pressure during the adjustment phase. Although some unavoidable plugging was detected in the oil burner nozzle, the self-cleaning mechanism (rapid manual stroking of the valve from full-shut to full-open removed obstructions) permitted steady-state runs of the desired length, 3 to 4 hours. At the present time, continuous overnight oil-fired operation is not proposed since flame safeguard systems have not been provided.

During the initial oil firing, furnace operation was not sufficiently long to collect and evaluate data at steady-state conditions. Therefore, from 28 March 1968 through 1 April 1968, the pilot plant was again warmed up on propane fuel. Oil was fired continuously from 1 April to 2 April to obtain the steady-state data given in Table 12. Characteristics of the No. 6 fuel oil burned are presented in Table D-1, Appendix D. Based upon the results of steady-state evaluation, the pilot plant was operating successfully within the design parameters. The pilot plant is now fully operational on both heavy oil and pulverized coal.

TABLE 12

GCA-RILEY COMBUSTION GAS GENERATING PILOT PLANT

Steady State Operational Data

Time: (4/2/68) 10:05 p.m.

CO_2	percent	13.0
O_2	percent	3.4
X.S. Air	percent	17
CO	percent	0
Sec. Air	SCFM	9.4 (11.9)*
Firing Rate	BTU/hour	40,000 (67,000)*
Cooling Air	SCFM	40
F.D. Fan Discharge	in. H_2O	40.3
Furnace Draft	in. H_2O	0.4
Flame Signal	arbitrary units	4.8
Oil Valve Set.	percent	4.5
Brick Temp.	°F	2008
Oil Temp. to Br.	°F	237
Oil Temp. Return	°F	237
Oil Press. to Br.	psig	6.3
A.H. Temp.	°F	495
Flue Gas Temp.	°F	295
Oil Temp. Suct.	°F	163
Dust Coll. Open		Yes
Elect. Prec. Open		No
Gas Press.	psig	--
Gas Flow	SCFM	--
Pilot on		No
Main Gas Br. On		No
Main Gas Br. On		Yes
F.D. Fan Inlet Temp.	°F	60 degrees
Test Chamber Press. Inlet	in. H_2O	1.0
Flue Gas Entering Air Heater	°F	1650 degrees
Flue Gas Just Inside Air Heater	°F	1358 degrees
Flue Gas Leaving Air Heater	°F	386
Burner Air Leakage as Determined by Air Heater Balance	SCFM	2.5

*Values corrected for air leakage

VI. CHAMBER REACTOR STUDIES

A. INTRODUCTION

A special irradiated reaction chamber has been constructed so that the behavior of flue gases generated by the pilot plant combustion system can be investigated under simulated field conditions. The basic experimental procedure will entail admitting to the chamber metered quantities of the stack effluent, cooled and diluted to gas concentration levels found at various downwind distances from the source. The loss of SO_2 will be studied as a function of concentrations of SO_2 and other molecular species, time, temperature, irradiation (flux, wavelength), humidity, concentrations of fly ash, liquid water, and SO_3 mist.

In these experiments, it is important that wall effects do not overwhelm free volume reactions. Therefore, the selected chamber volume is fairly large, 42.3 cubic feet, so that with a compact form the surface-to-volume ratio could be minimized, 1.82 feet^{-1} vs. 1.39 feet^{-1} and 1.72 feet^{-1} for spheres and cubes of equivalent volume, respectively.

B. CHAMBER DESIGN

A commercially available upright freezer unit*, Figure 7, which satisfied the above dimensional requirements was selected as the basic reactor structure. Several modifications and additions to the equipment were made, however, to satisfy experimental needs. These included the provision of glass inspection doors, temperature controls, special gasketing to prevent leakage, several test ports for sample collection, an 8-inch diameter ultraviolet transmitting window, and front surface plane mirrors in contact with the two opposing side walls. It is planned to line all interior side walls (presently aluminum) with "Trifoil", a Teflon-coated aluminum foil to minimize wall adsorption of gaseous constituents. A mixing fan will also be installed to provide uniformity in gas concentrations during tests.

The function of the plane front surface mirrors is to permit several reflections of the irradiating beam of the solar simulator (500 watts) so that the chamber volume sees essentially a normal solar flux (1400 watts per square meter). Further details on chamber design features and auxiliary equipment and a schematic drawing of the chamber assembly are given in Appendix E.

C. RESULTS

Preliminary sampling instrument checks were carried out with a Perkin-Elmer Model 357 infrared spectrometer (2 to 25 microns). Further discussion of the IR system is given in Appendix E. A mixture of 20 ppm SO_2 in ambient air was drawn continuously from the reaction chamber and its spectral absorbence determined over the wavelength range

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*Nor-Lake Model F43C, Hudson, Wisconsin

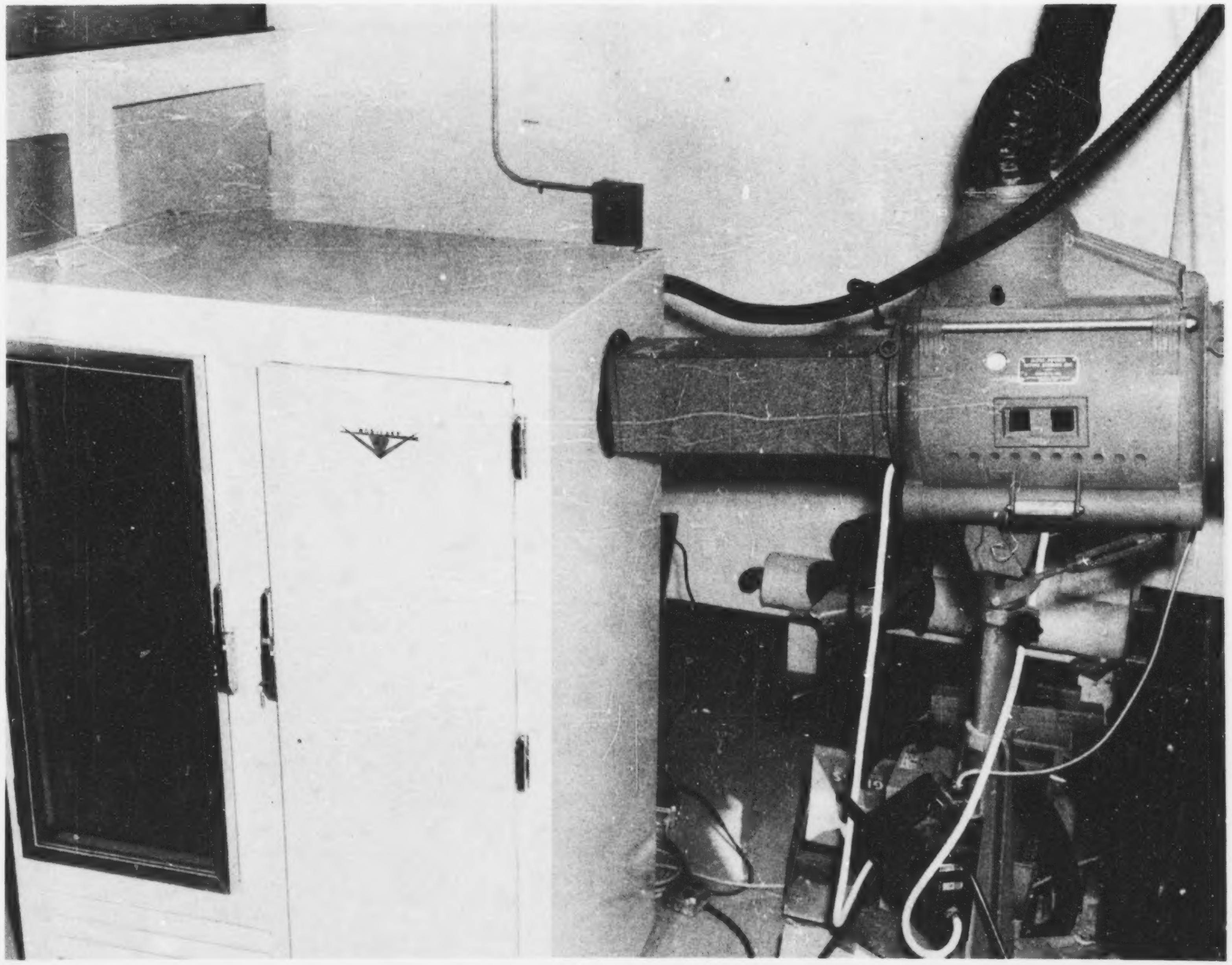

Figure 7a. Reaction chamber and solar simulator.

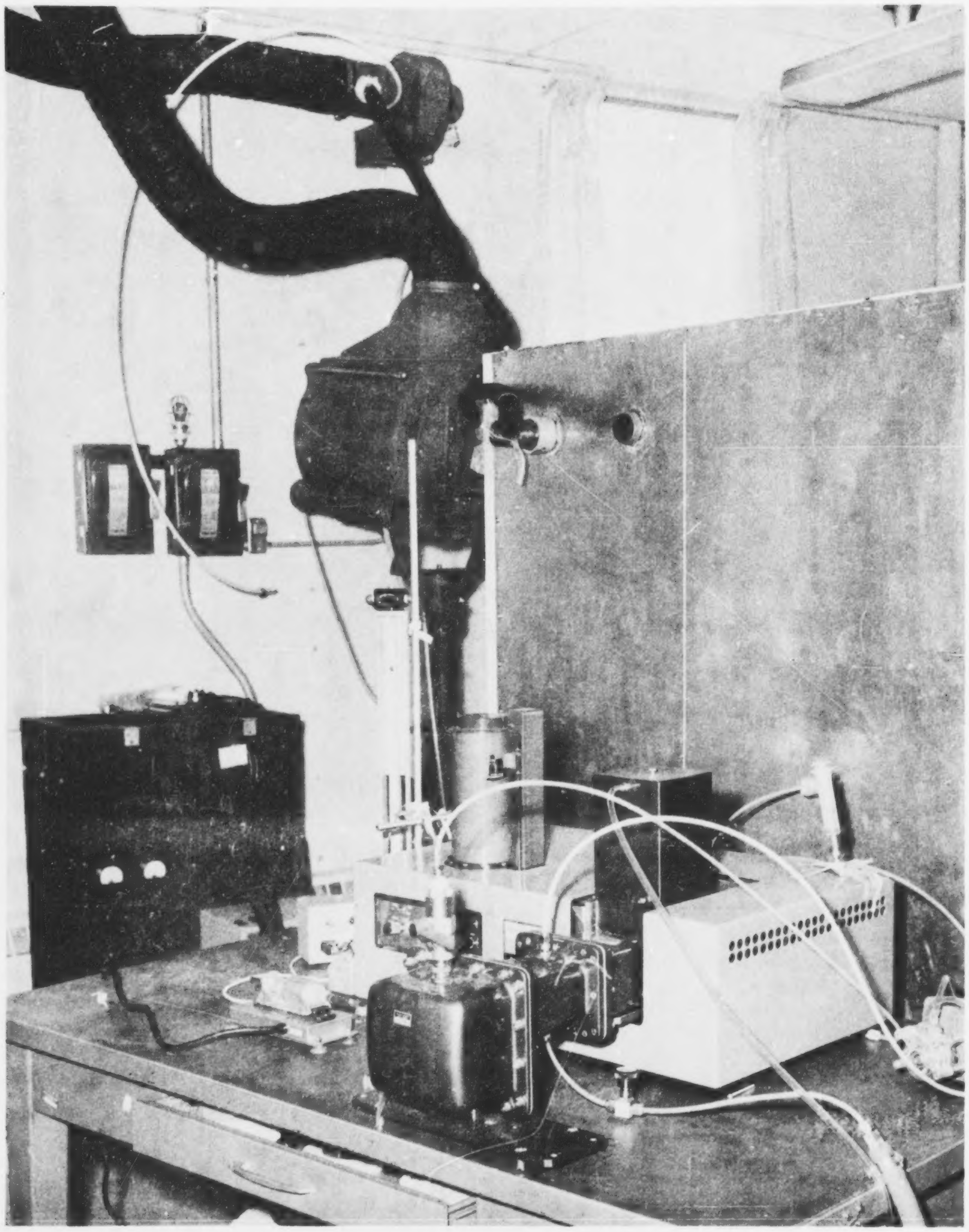

Figure 7b. Reaction chamber and IR sampling assembly.

2.5 to 8.0 microns. According to test results shown in Figure 8, this system will detect SO_2 in the ppm range in the presence of ambient levels of CO_2 and water vapor, and will provide the required sensitivity for the scheduled experiments.

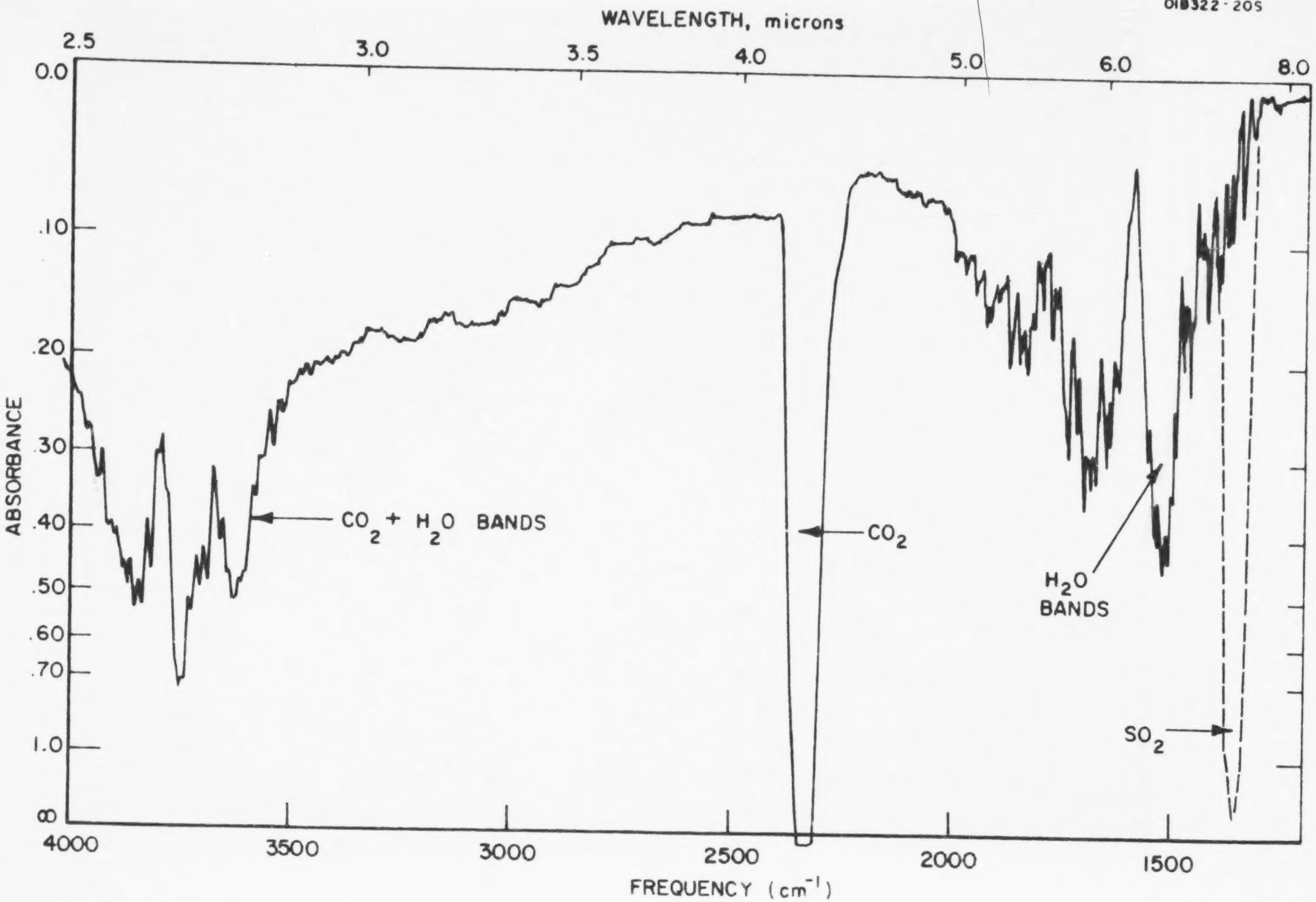

Figure 8. Infrared spectrum of SO_2 and chamber background constituents.

VII. LABORATORY STUDIES - CHEMICAL REACTION STUDIES

A. INTRODUCTION

The purpose of the laboratory studies discussed in this section is to investigate on a bench scale several alternative mechanisms which, singly or in combination, may contribute to observed losses of sulfur dioxide from power plant plumes. Mechanisms presently under consideration include photo-oxidation to SO_3 by solar radiation in the near ultraviolet (approximately 3000 to 3400Å); solution in small water droplets present in the atmosphere at high humidity; and homogeneous or heterogeneous reactions involving moisture and other constituents or catalysts in fly ash. The role of these and other possible mechanisms in the cycle of the atmospheric sulfur compounds has been studied by several investigators (Ref. 10-12).

Present estimates of the half life of SO_2 in the atmosphere (assuming that the chemical decay of SO_2 takes place as a simple exponential process) range from two hours to several days (Ref. 13 and 14). Although the more rapid decay is associated with high atmospheric moisture contents, less than 0.01 percent of the free SO_2 would be expected to go into solution according to equilibrium solubility in pure water (assuming a nominal liquid content of 1 gram/m^3). Hence, the presence of a wide variety of atmospheric particulates (mineral or organic) which may act as condensation nuclei (Ref. 10) presumably accounts for increased absorptive capacity of liquid droplets. Ordinary fly ash through its buffering and neutralizing characteristics (Ref. 14 and 15) and catalytic substances such as $MnSO_4$ and $FeSO_4$ (Ref. 16) have been reported to increase the capacity of aqueous sinks.

Several heterogeneous reactions may take place upon the extended particulate surface, 10^4 cm^2/gram of power plant fly ash emissions at concentrations of 0.03 grains/ft^3 (Ref. 17). The presence of numerous metallic oxides, vanadium and nickel in relatively large amounts (approximately 3 percent in some oil ashes) and trace quantities of several catalytically active transitional elements serve to enhance SO_2 oxidation (Ref. 17-19)

B. PHOTOCHEMICAL OXIDATION

1. Background

A review of photochemical oxidation processes pertaining to sulfur dioxide indicates that several atmospheric reactions may contribute to SO_2 losses from stack plumes. The absorption spectrum of SO_2 in the 2400 to 3900Å region arises from two electronic excited states. The first absorption band associated with the first excited state has its origin at 3880Å with a maximum intensity at 3740Å. The absorption due to the second excited state is of primary interest in the photochemistry of SO_2 in the atmosphere and extends from 3376Å to 2400Å with a maximum at 2940Å (Ref. 20). The intensity of this transition is fairly strong as can be seen in Figure F-1, Appendix F (Ref. 21). Only a small fraction of the solar radiation of wavelengths shorter than 3000Å reaches the surface of the earth as a consequence of absorption by ozone in the upper atmosphere. To the best of our knowledge, the absorption of SO_2 is very weak in the 3400 to 3900Å regions and should not lead to significant photodecomposition rates (Ref. 22).

The solar absorption coefficients for SO_2 per 100Å interval and the values of the solar flux (Ref. 23) are shown in Figure F-2, Appendix F as a function of wavelength. The calculated excitation function (the product of the solar flux and the SO_2 absorption coefficient) is presented in Figure F-3, Appendix F as a function of wavelength. It appears that the maximum excitation yield may be expected to occur at 3100Å and not at longer wavelengths. In spite of the higher solar flux at longer wavelengths, the SO_2 absorption coefficient decreases rapidly.

A study of those photolytic processes which are considered prime factors in the formation of photochemical smogs suggests that reaction rates at low concentrations are too slow to account for significant SO_2 losses in stack plumes. The above concept is subject to controversy, however, since many photochemical reactions having the potential to produce more rapid SO_2 decay have not been investigated thoroughly. Consequently, the main effort in the first part of the program has been directed toward the study of photolytic processes. Various mixtures of SO_2 and O_2 from 100 percent to 60 percent SO_2 were irradiated in a flow reactor so that reaction products which might absorb uv irradiation could be removed from the system. Quantum yields determined with excitation at 2537Å and 3130Å were in general agreement with those reported by other investigators. Based upon an extrapolated value of 0.04 for the quantum yield at 3130Å, an SO_2 decay rate of 2.4 percent/hour was calculated. At this level, the uncatalyzed homogeneous photochemical formation of SO_3 becomes a significant factor in plume decay.

2. Test Apparatus and Procedures

Previous studies have shown that the major product formed by the photolysis of SO_2 is SO_3. Photochemical decomposition of SO_2-O_2 mixtures has been observed in static systems by measuring the change in SO_2 concentration with time. In the present study, a flow system has been employed in which SO_3 is continuously removed from the absorption region, thus minimizing interfering absorption of light which could lead to side reactions. This study considers the quantum yield of SO_3 formation in pure SO_2 and in SO_2-O_2 mixtures (down to 60-percent SO_2). Details on the flow reactor concentration, sampling and analytical procedures for SO_3, uv light source, calibration techniques for measurement of photon flux, and transmission characteristics for filter and windows are discussed in Appendix F.

3. Results

Several background experiments were performed to establish the operating parameters of the flow reactor, Figure F-4, Appendix F. Since the rate of SO_3 formation in the absence of uv excitation was found to vary directly with test duration (flushing time), accurate correction could be made for SO_3 generated by processes other than photolytic, Figure F-5, Appendix F. Based upon $SO_4^=$ analyses performed by the barium chloranilate technique and the application of the blank correction for dark SO_3 formation, Figure F-5, the amount of $SO_4^=$ produced under unfiltered Hg arc excitation also varied directly with photolysis time Figure F-6, Appendix F.

Quantum yields determined for pure SO_2 and SO_2-O_2 mixtures in two wavelength regions, 2900 to 3130Å and 2537Å, are indicated in Figure 9. The quantum yield is defined as the number of molecules formed per number of quanta absorbed for any arbitrary irradiation period. Chemical analyses for sulfate formation and ferrioxalate actinometry for light flux intensity provided the information for calculating quantum yields. Sulfur dioxide concentrations less than 60 percent could not be studied in the present equipment since light absorption was incomplete below this concentration level. For pure SO_2, the quantum yield was approximately the same at 3130Å and 2437Å, i.e., 0.053 and 0.068, respectively. In 60-40 SO_2-O_2 mixtures, the quantum yield increased by a factor of approximately four at 3130Å and 2537Å to 0.22 and 0.29, respectively.

In order to determine the effect of the radiation intensity at 2537Å on the quantum yield, photochemical sulfate formation with the unfiltered lamp was compated to the sulfate formation with the 2537Å filter. After the SO_3 formation for the unfiltered arc was corrected for the amount of SO_3 from the other mercury lines, good agreement was obtained between these results with no functional dependence of yield on light intensity.

After a five or ten-minute irradiation of SO_2 with the unfiltered mercury arc, a yellow, water-insoluble deposit was observed (Ref. 24). The yellow deposit (possibly sulfur) was very soluble in CS_2, but sufficient material could not be obtained even with several irradiations to determine the infrared spectrum. No noticeable fogging was observed at 2537Å and 3100Å, so that no correction was necessary.

Preliminary runs were also performed in which irradiated SO_2 gas was bubbled through various absorbing solutions, e.g., distilled water, sodium hydroxide, etc., to determine the nature of possible reaction products other than SO_3. The solutions were tested for sulfide, thiosulfate and sulfate ions using classical microanalytical techniques. However, only sulfate ions were found (Ref. 25).

4. Discussion

The results of photolysis studies by Chen (Ref. 26) have also been shown in Figure 9 for similar gas mixtures and irradiation conditions. A review of Chen's experiments indicated that light absorption by SO_2 in his system was incomplete and that he apparently did not correct for this loss. Chen's quantum yields, if corrected, would be higher than those shown in Figure 9. It is not clear, however, why his quantum yields did not decrease at low SO_2 concentrations.

In Table 13 quantum yields obtained in this study are compared to those determined by other investigators. Our results exhibit general agreement with these data, taking into account the fact that higher quantum yields were expected at the higher concentration levels used in our experiments.

The basic chemical reactions considered in the mechanism of SO_2 photo-oxidation are listed in Table 14. In contrast to the absorption region below 2000Å where many primary processes occur (Ref.24), the absorption of light by SO_2 in the 2400 to 3400Å region leads only to the formation of electronically excited SO_2 (SO_2^*). In pure SO_2, SO_3 formation occurs only by Reaction 2. The deactivation of the excited SO_2 by ground state molecules (Reaction 1) is the predominant process and results in a low quantum yield. The initial increase in quantum yield as oxygen is added is the result of Reactions (3), (4), and possibly (6). As the oxygen concentration is increased further, Reaction (3) followed by (4) becomes predominant. Assuming no deactivation of SO_2^* (in oxygen), this process could lead to a maximum quantum yield of 2, i.e., 2 molecules of SO_3 formed per quantum absorbed.

An empirical relationship obtained from the data presented in Figure 9 describes the quantum yield of SO_3 formation as a function of SO_2 concentration in O_2 (60 to 100 percent SO_2) and is expressed as:

$$\phi_{SO_3} = \phi^* \left[\frac{1 + 5.21 \left(\frac{O_2}{SO_2} \right)}{1 + 0.183 \left(\frac{O_2}{SO_2} \right)} \right]$$

where ϕ^* = quantum yield of SO_3 formation in pure SO_2.

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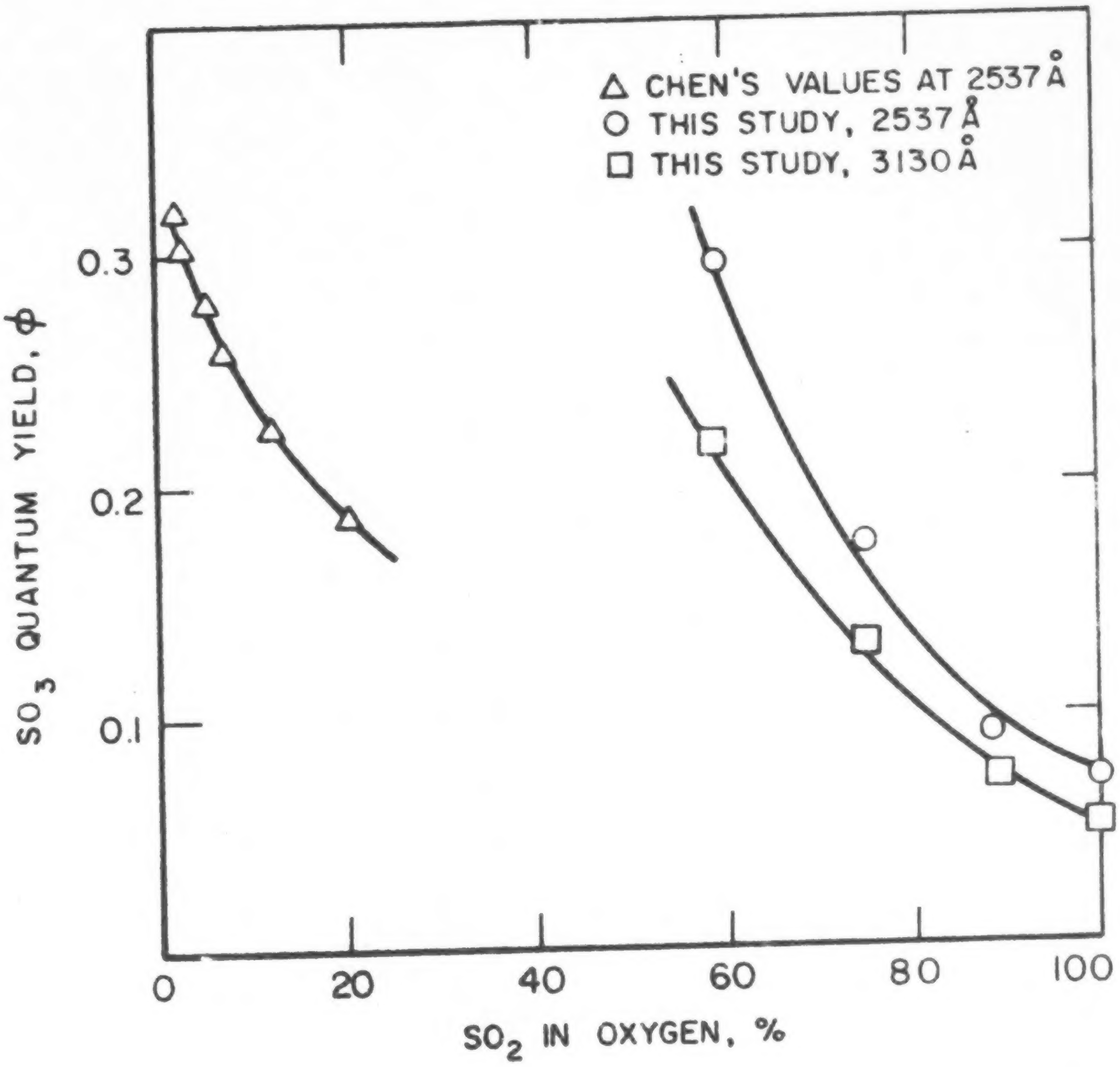

Figure 9. Quantum yields of SO_3 formation.

TABLE 13

QUANTUM YIELDS OF SO_3 FORMATION

φ(λ)		Conditions	Reference
3100Å	2537Å		
	0.18-0.30 0.68	2-8% SO_2 + Air Hg Sensitized	Chen, S.W., Acta Chemica Sinica, 24, 187 (1958)
10^{-2} or 10^{-3}		SO_2 in Air	Blacet, F.E., Ind. Eng. Chem., 44, 1339 (1952)
0.036		SO_2 + Air Reduced Pressure	Hall, T.C., Ph.D. Thesis, Univ. of Calif.(L.A.)(1953)
Small	0.01	SO_2 + O_2 Various Mixtures	Kornfeld, G, and Weegmann, E., Z. Electrochem 36, 789 (1930)
0.3		SO_2 (several ppm) + Air	Renzetti, N.A., and Doyle, G.T., Intern. J. Air Pollution 2, 327 (1960)
3×10^{-3}		SO_2 (several ppm) + Air	Gerhard, E.R. and Johnstone, H.F., Ind. Eng. Chem. 47, 972 (1955)
0.053	0.068	Pure SO_2	This Study
0.22	0.29	SO_2 + O_2 (60:40V/V)	

From the elementary reactions of Table 14 at steady state, the theoretical quantum yield of SO_3 formation is:

$$\Phi_{SO_3} = \frac{1}{1 + \frac{k_1 + k_2}{k_3} \frac{SO_2}{O_2}} \left[\left(1 + \frac{k_2\ (SO_2)}{k_3\ (O_2)} \right) + \left(\frac{k_4 (SO_2)}{k_5\ (O_2)} \right) \left(\frac{1}{1 + \frac{k_4 (SO_2)}{k_5\ (O_2)}} \right) + \left(\frac{k_6\ (O_2)}{k_6 (O_2) + k_7} \cdot \frac{k_2 (SO_2)}{k_3\ (O_2)} \right) \right]$$

Preliminary analysis of this equation indicates that a maximum value of Φ_{SO_3} may occur in the neighborhood of 15-percent SO_2. At lower SO_2 concentrations, Φ_{SO_3} is expected to decrease as a consequence of the competition for oxygen atoms caused by ozone formation (Reaction 5). For concentrations of SO_2 below 10 percent (and since $k_5/k_4 \approx 0.1$) (Ref. 27), the above expression for ΦSO_3 approaches unity since a term for the deactivation of SO_2^* by O_2 has not been included.

An alternative mechanism has been suggested which proceeds through an SO_4 intermediate, as follows:

$$SO_2^* + O_2 \longrightarrow SO_4$$

$$SO_4 + O_2 \longrightarrow SO_3 + O_3$$

$$SO_4 + SO_2 \longrightarrow 2(SO_3)$$

This mechanism leads to similar products and similar functional dependence of ΦSO_3 as the proposed mechanism although the existence of the postulated intermediate remains to be shown.

An estimate of the uncatalyzed photochemical oxidation rate of SO_2 in a plume has been made on the basis of a quantum yield of 0.04 at 3130Å. This is the lowest value of the quantum yield observed at 3130Å in pure SO_2. The quantum yield at low concentrations of SO_2 (say 1 part per million) may be of this order. The SO_2 concentration and the plume dimensions were calculated at 8 miles from the stack. A square-well concentration of 10 parts per million SO_2 and 300-foot pathlength was substituted for the expected normal distribution. The integrated flux absorbed was calculated using the absorption coefficients of SO_2 given by Leighton (Ref. 28) and the approximate noonday solar spectrum given by Renzetti and Doyle (Ref. 29). These data yield a value for the SO_2 oxidation rate of 2.4 percent $hour^{-1}$ ($k = 10^{-3}\ sec^{-1}$). For these values the uncatalyzed homogeneous photochemical SO_3 formation becomes a factor of significance in plume decay.

TABLE 14

ELEMENTARY REACTIONS IN THE PHOTO-OXIDATION OF SO_2 AT 2537 OR 3100Å

$$SO_2 \xrightarrow{h\nu} SO_2^{*} \qquad (\lambda = 2400\text{-}3200\text{Å})$$

$$\begin{tikzcd}
(1) & SO_2^{*} + SO_2 \arrow[r, "k_1"] \arrow[dr, "k_2"] & 2\ SO_2 \\
(2) & & SO_3 + SO
\end{tikzcd}$$

(3) $SO_2^{*} + O_2 \xrightarrow{k_3} SO_3 + O$

(4) $O + SO_2 \xrightarrow{k_4} SO_3$

(5) $O + O_2 \xrightarrow{k_5} O_3$

(6) $SO + O_2 \xrightarrow{k_6} SO_3$

(7) $SO + \text{wall} \xrightarrow{k_7} SO\ \text{lost}$

C. HETEROGENEOUS OXIDATION OF SULFUR DIOXIDE IN WATER

It was indicated previously that the rate of absorption of SO_2 gas in liquid water droplets in the atmosphere depends upon reactions in the liquid phase controlled by the presence of catalysts or appropriate ions. A simple flow system for the preparation of low concentrations of SO_2 in air was utilized for study of the catalyzed oxidation of SO_2 in water. Samples of the solution were removed periodically, flushed with nitrogen to remove dissolved SO_2, and analyzed for $SO_4^=$ by the barium chloranilate method.

The measurements of Junge and Ryan (Ref. 15) on the oxidation of SO_2 in the presence of $FeC\ell_2$ catalyst have been repeated and their observations were confirmed. The $SO_4^=$ concentration increased almost linearly with time until pH 2.2 was reached (4 hours). No further conversion of SO_2 to $SO_4^=$ was observed after this time. At these low concentrations of SO_2 (17 parts per million) little oxidation was observed in the absence of a catalyst as indicated in Figure 10.

A sample of aged NBS test dust (Potomac Electric Power Co. fly ash) was examined for catalytic effect and found to be relatively inactive compared to $FeC\ell_2$. No attempt was made to determine dissolved iron or basic ions in the final solution. Freshly collected samples of fly ash (1 to 2 days old) and fly ash aged approximately 3 months were obtained from the pulverized coal-fired Salem Harbor Station (NEES). The catalytic activity of these samples in aqueous solution was found to be at the same low level as that of the NBS fly ash. The time dependence of pH in suspensions of these three fly ash samples is shown in Table 13. The very old P.E.P. Co. (NBS) fly ash exhibited little change in pH from its initial value of about 8. Fresher samples from the ash hoppers at Salem Harbor Station were initially much more alkaline and upon standing approached the pH values of 12 reported by Gartrell (Ref. 1). The freshest sample (1 to 2 days old) showed considerable change in pH with time increasing from 9.5 to 11.2 during 5 hours.

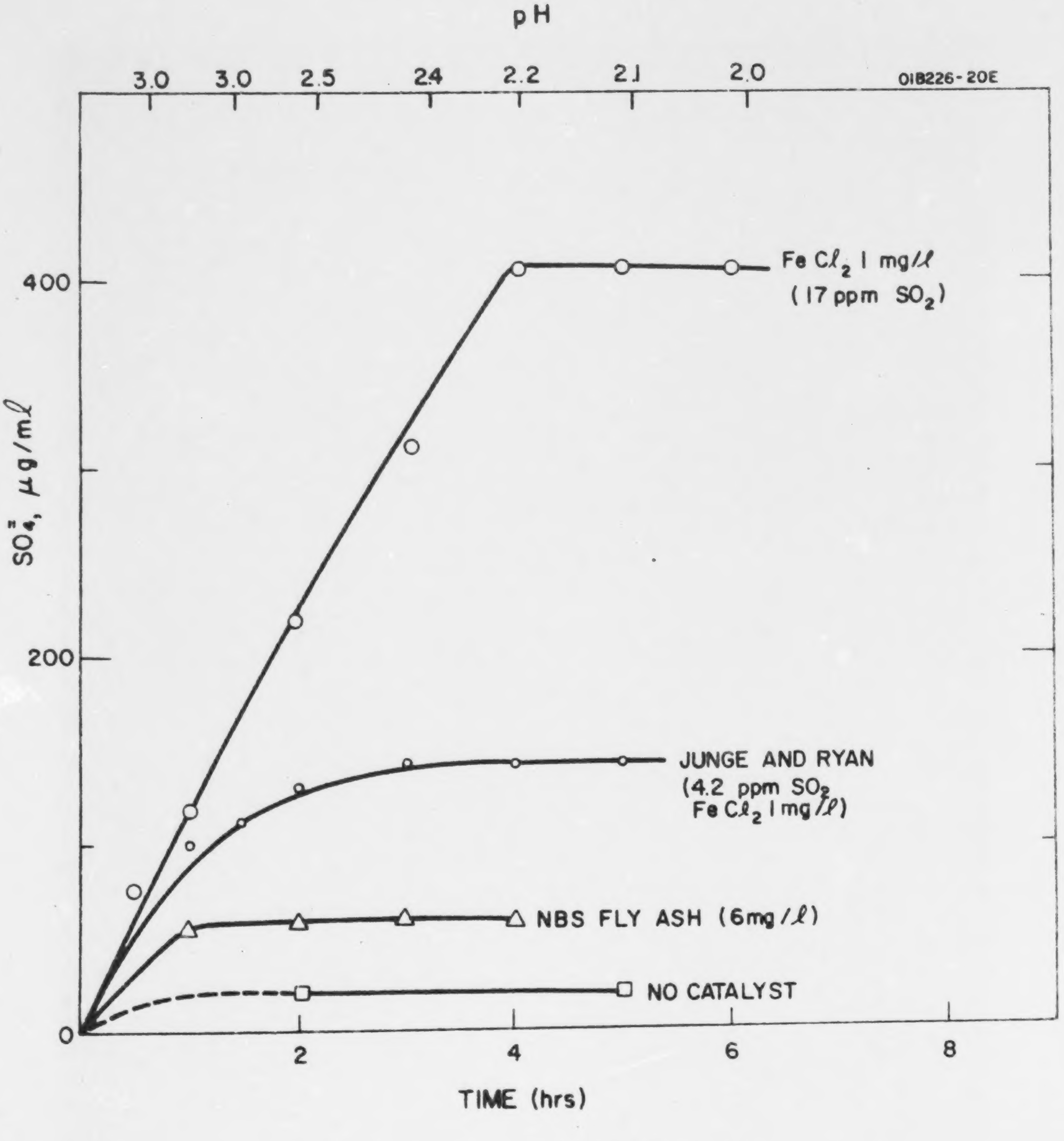

Figure 10. SO_2 aqueous oxidation rates.

TABLE 13

CHANGE IN pH OF FLYASH SUSPENSIONS[a] IN WATER

	Time (hours)	pH	Type of Flyash
(1)	0	8.0	PEPCO-NBS (aged years)
	0.5	8.2	
	1.5	8.15	
	2.5	8.15	
	5.0	8.0	
(2)	0	10.7	Salem Harbor (aged 3 months)
	0.5	11.2	
	2.0	11.2	
	3.0	11.2	
(3)	0	9.5	Salem Harbor (aged 1 or 2 days)
	1.25	10.5	
	2.25	10.55	
	5.0	11.2	

[a] 1 gram flyash per 10 milliliters water

VIII. PLUME MODELING

A. INTRODUCTION

One objective of the field program is to determine empirically the form of the decay function of SO_2 which occurs within the atmosphere as a result of such processes as adsorption, absorption or conversion of SO_2 to other chemical species. The experimental technique, described in Section III, consists of introducing an inert tracer, SF_6, into the plume and determining the SO_2/SF_6 concentration ratio by direct measurements over travel times approximately the half-life of SO_2, if possible. The decay rates determined during a series of flights are to be correlated with plume characteristics and atmospheric conditions. Any relationships found are to be compared with theory and the results of laboratory experiments in an effort to establish appropriate decay rates for various meteorological conditions, different power plants, and different fuels. Once established, these decay functions can be incorporated into diffusion models.

B. DESCRIPTION OF THE MODEL

The diffusion model most commonly used to calculate the concentration field downwind from a continuous point source assumes mass continuity and a Gaussian distribution of material along the lateral and vertical axes of the plume. When modified to account for reflection of effluent from the earth's surface, this Gaussian plume model is defined by the expression:

$$\chi(x,y,z) = \left(\frac{Q}{2\pi\sigma_y\sigma_z\bar{U}}\right)\exp\left(-\frac{y^2}{2\sigma_y^2}\right)\left[\exp\left(-\frac{(z+h)^2}{2\sigma_z^2}\right)+\exp\left(-\frac{(z-h)^2}{2\sigma_z^2}\right)\right] \quad (1)$$

where χ = concentration expressed as mass per unit volume

Q = source strength expressed as mass per unit time

$\bar{U}$ = mean transport speed of the wind

h = effective height of release above the ground plane

σ_y, σ_z = standard deviations of the crosswind and vertical concentration distributions

x, y, z = downwind, crosswind, and vertical coordinates, respectively.

The crosswind and vertical plume dimensions σ_y, σ_z are usually defined in terms of simple power-law functions of downwind distance of the form

$$\sigma_y = \sigma'_A \, x_r \left(\frac{x}{x_r}\right)^{\alpha}$$

$$\sigma_z = \sigma'_E \, x_r \left(\frac{x}{x_r}\right)^{\beta}$$

where σ'_A and σ'_E are, respectively, the standard deviations of wind azimuth and elevation angle in radians and x_r is a unit reference distance.

The above Gaussian plume model may be modified further to provide for reflection from the base of a thermally - stable layer and for restrictions to horizontal plume expansion due to topographical features. It may also be adjusted for source dimensions by introducing virtual distance concepts.

The most commonly accepted procedure for incorporating a decay factor into a diffusion model is to assume an exponential decay. In this case, the concentration after time t is given by the expression

$$\chi = \chi_o \exp(-kt) \tag{2}$$

where χ_o is the concentration predicted by a model such as the one described above, without regard to decay, and the constant k is related to the half-life τ by

$$k = \ell n \, 2/\tau \tag{3}$$

When concentration is expressed as a function of distance x, the substitution $x/\overline{U} = t$ is made. Although a first order oxidation reaction has been confirmed by Gerhard and Johnstone (Ref. 31) for photochemical oxidation of SO_2, the reaction rate may be psuedo-first order, or possibly of higher order, for liquid phase oxidation or heterogeneous catalytic reactions on fly ash. In any case, the form of the decay fundtion cannot be assumed a priori to be exponential.

C. USE OF THE MODEL FOR FLIGHT PLANNING PURPOSES

As pointed out in Section VI current estimates of the half-life of SO_2 within the atmosphere range from several days to a few hours and suggest that a successful field investigation of decay rates within power plant plumes will require plumes that can be tracked over travel times of at least two hours. Such plumes occur occasionally in the Boston area during the fall months when the stack gases are released into a stable atmosphere and are carried out over the water by steady winds of 10 to 15 mph. Sampling over water offers advantages in that flight restrictions are minimal, and there are no significant sources downwind from the stacks. For use in planning the flight sampling program, a simplified model was constructed to describe plumes from the Weymouth and Salem power plants under these ideal meteorological conditions.

In the model, it is assumed that the plant effluent is emitted at the same rate from three stracks of equal height spaced at 50-foot intervals along a line normal to the mean wind direction. This configuration approximates the geometry at the two plants during periods of westerly winds. In the model calculations, the plumes from the three stacks were treated individually near the source, and the distance at which the plumes merged was calculated using appropriate expansion rates. For this purpose, the three plumes were considered to have merged when the concentration across the composite plume became essentially invariant between the alongwind axes of the two outer plumes. It was assumed that each plume was initially 8 meters in diameter at a distance of 5 meters from the stack and a virtual distance x_y, corresponding to this lateral plume dimension, was calculated from the general expression for lateral expansion

$$\sigma_y = \sigma_A' \, x_r \left(\frac{x + x_y}{x_r} \right)^{\alpha} \qquad (4)$$

where σ_A' = standard deviation of the azimuth wind direction in radians

x_r = unit reference distance

and α = lateral diffusion coefficient

Values of the input parameters used in the solution of Equation (4) were: σ_y = 1.86 meters, σ_A' = 0.017 radians, α = 0.9, and x = 5 meters. Using the virtual distance of 179 meters thus calculated, Equation (4) was solved again for the distance at which the plumes merged by setting $\sigma_y = 1/1.15\ (d/2)$, where d is the distance between adjacent plume axes. This approximate relationship is based on the Gaussian distribution in which the concentration falls to one-half the peak value at a distance of 1.15 σ from the plume axis. Under these assumptions, the plumes merged at a distance of 0.36 miles from the stacks. The standard deviation for the composite plume at this distance was taken as 13.7 meters, the separation distance of the outer plume axes plus 4.3 σ_y, where σ_y refers to the plume from a single stack. At distances beyond 0.36 miles, it was assumed that the composite plume was Gaussian and the value of α was 0.85. The vertical diffusion coefficient β was set equal to 0.9 near the source, but was assumed to decrease with increasing downwind distance. The model estimates of σ_y and σ_z for the three-stack plant are shown in Figure 11 for distances from 0.5 to 50 miles.

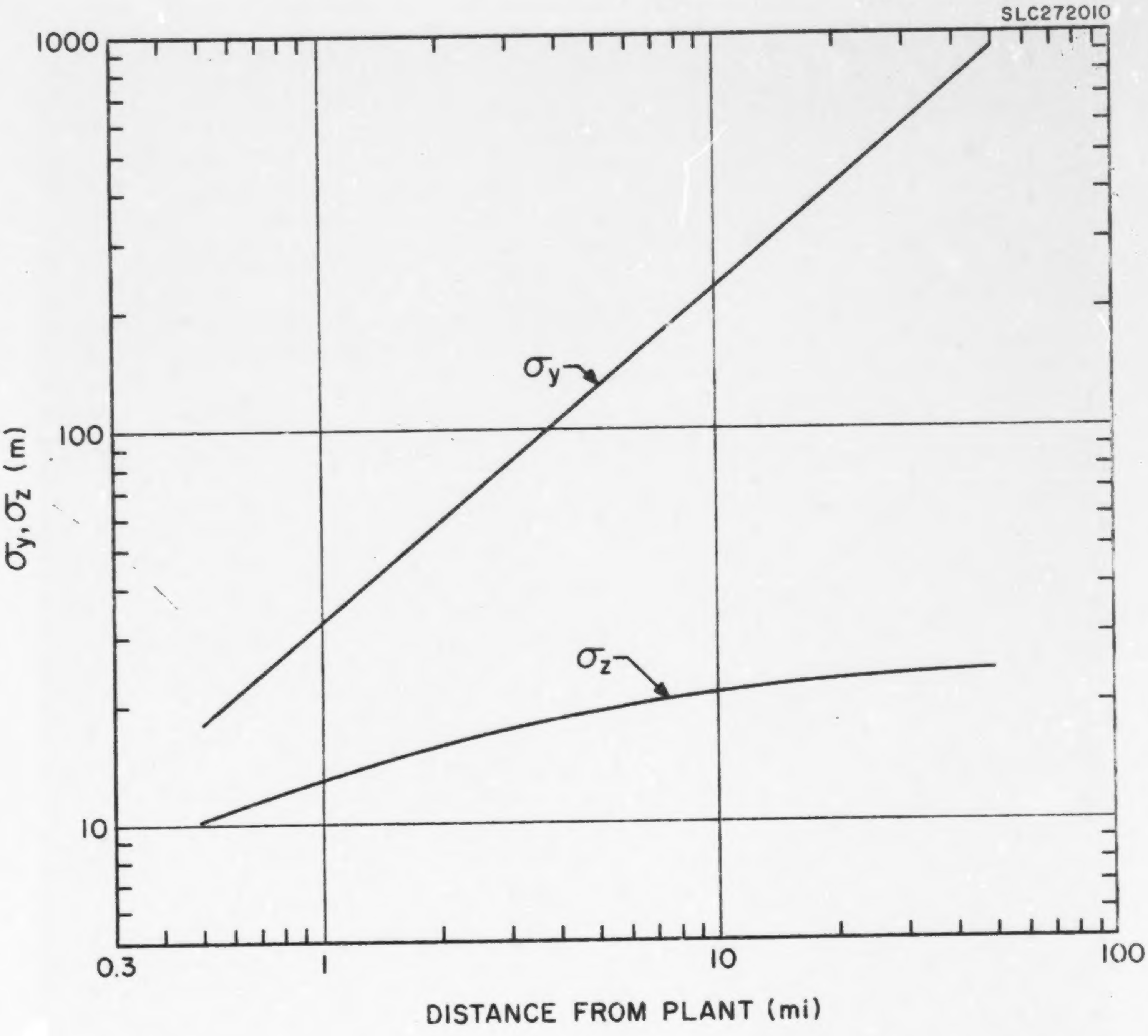

Figure 11. Estimates of the standard deviations of the crosswind concentration σ_y and of the vertical concentration σ_z at various distances downwind from the Weymouth and Salem plants under very stable conditions.

With the restricted vertical growth illustrated in Figure 11, plumes released at the Weymouth and Salem plants (effective release heights of the order of 500 feet) will remain above the water surface during the 50-mile travel distance under consideration. In this case, normalized axial concentrations can be calculated from the Gaussian plume expression

$$\chi_a = \frac{Q}{2\pi \sigma_y \sigma_z \overline{U}} \tag{5}$$

The curve of normalized axial concentration as a function of distance, shown in Figure 12, was calculated from this expression using values of σ_y and σ_z obtained from Figure 11. Finally, the normalized curve of Figure 12 was used with a mean wind speed of 5 m/sec and source strengths of 705 and 1080 grams/sec, respectively, to estimated axial concentrations downwind from the Weymouth and Salem plants. The results, expressed in milligrams per cubic meter, are shown in Figure 13.

During the field program, no flights were made under the very stable conditions modeled in Figures 11, 12, and 13.

D. USE OF THE MODEL TO CHECK THE CONSISTENCY OF FIELD DATA

The most complete definition of a plume cross section obtained during the field program is provided by the 12 traverses made at elevations between 400 and 1900 feet at a distance of 1.85 miles from the Salem plant during the flight of 20 January 1968. The consistency of the measurements of plume dimensions and axial concentration made at this distance were checked using the Gaussian plume equation (5). Wind speed during the flight was approximately 15 mph, and the lapse rate between 500 and 1500 feet was approximately equal to the dry adiabatic. Estimates of plume width and depth were made from the plume cross section shown in Figure C-1 which was prepared from recorder traces corrected for response time by procedures outlined in Appendix C. From this figure, the plume width was estimated to be 0.44 miles and the plume depth to be 1600 feet. Examination of the SO_2 traces obtained during the cross plume passes suggested that the observed plume dimensions were approximately bounded by the one-tenth peak concentration values. In this case, with a Gaussian distribution, the observed width and depth are equal to 4.3 σ_y and 4.3 σ_z, respectively. Model input values, in consistent units, are: σ_y = 165 meters, σ_z = 113 meters, and $\overline{U}$ = 6.7 m/sec. A value of 5.9×10^5 milligrams/sec was used for the source strength Q in agreement with measurements made at the two stacks which were in operation at the time of the flight. When substituted in Equation (5), these values yield a peak concentration of 0.75 milligrams/m^3, or approximately 0.27 parts per million. This calculated peak value is somewhat greater that the higher observed concentration of about 0.18 shown in Figure C-3. Because of the response characteristics of the SO_2 recorder,

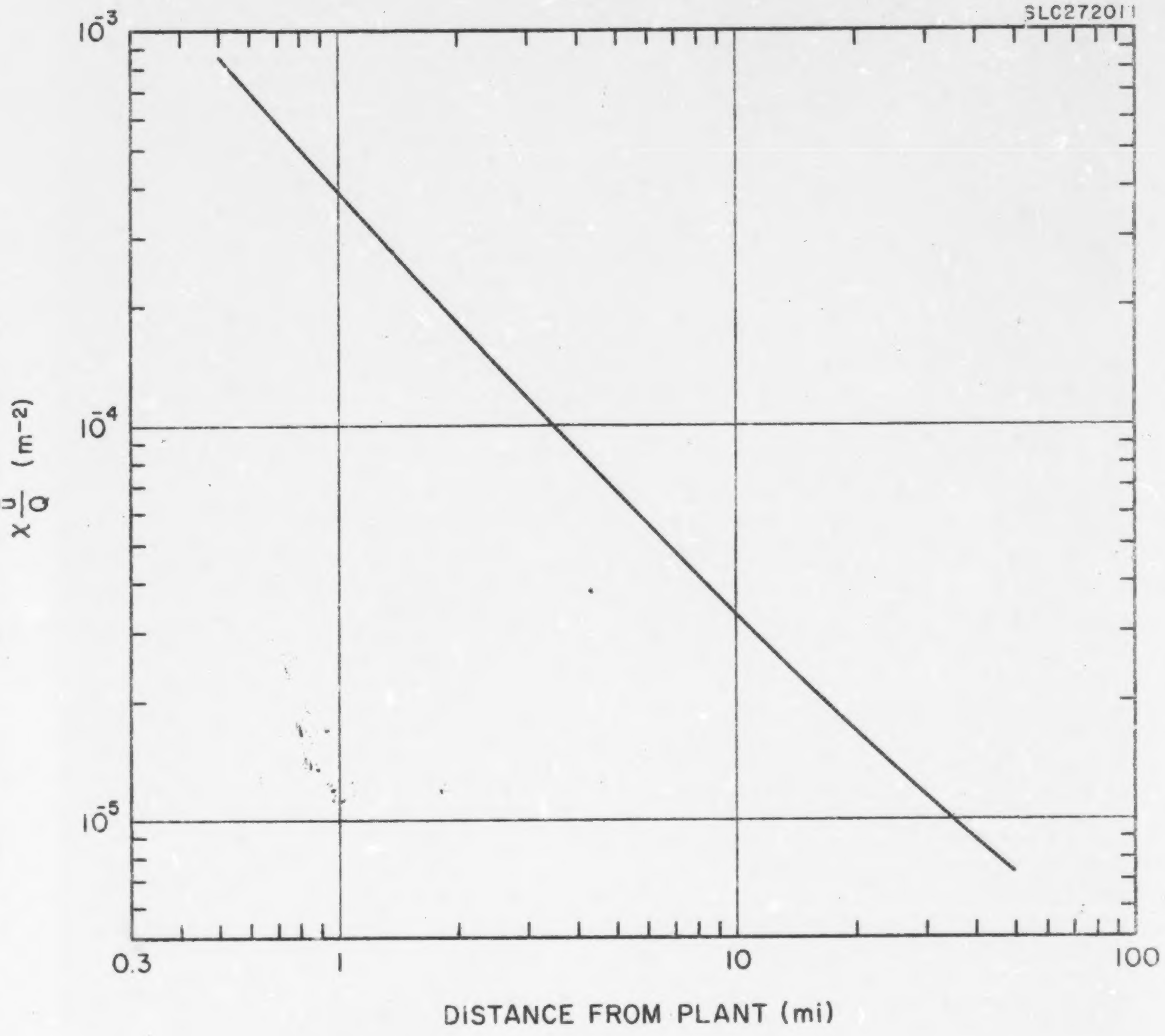

Figure 12. Estimates of the normalized axial concentration $X(\overline{U}/Q)$ at various distances downwind from the Weymouth and Salem plants under very stable conditions.

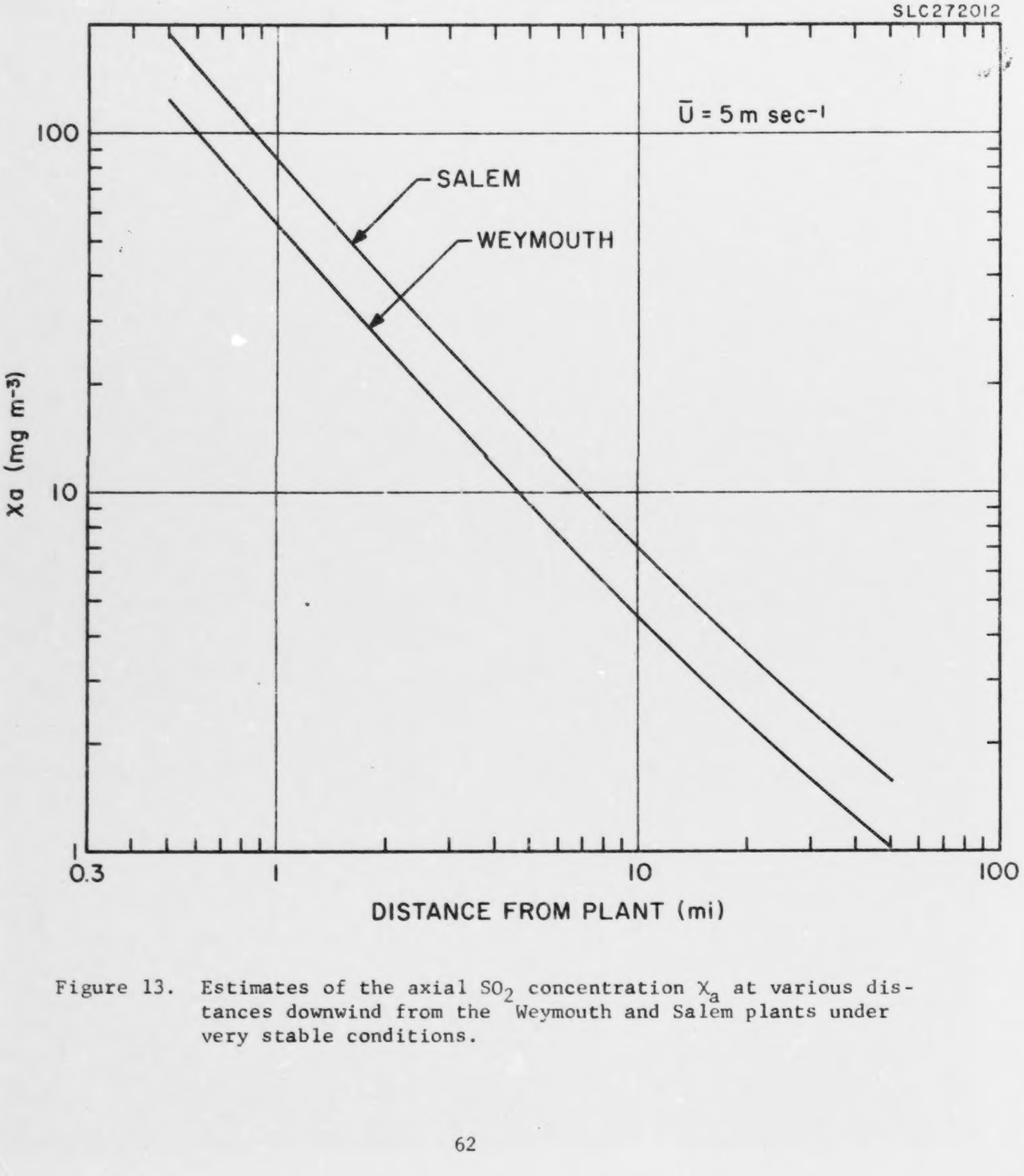

Figure 13. Estimates of the axial SO_2 concentration χ_a at various distances downwind from the Weymouth and Salem plants under very stable conditions.

the observed concentration is an underestimate of the true concentration. In view of the necessary approximations, the measurements of plume dimensions and concentration at 1.85 miles are considered to be consistent with the Gaussian model.

IX. FUTURE STUDIES

A. FIELD PROGRAM

During the second year program emphasis will be placed on the description of plume behavior and, in particular, upon the measurement of SO_2/SF_6 ratios at several downwind plume locations. Thus, it is proposed that the original schedule be reviewed to include approximately 25 hours of aircraft measurements as part of the second year effort. Tests will be performed in accordance with first year procedures with emphasis upon improved sampling and analytical procedures to measure SO_2 and SF_6 concentrations within the plume.

B. LABORATORY STUDIES

1. Chamber Reaction Studies

The pilot plant flue gas generating facility will be utilized to furnish realistic stack gas effluents for reaction chamber studies of simulated stack plumes. Selective studies will be conducted in which SO_2, NO_x, hydrocarbons, and other typical flue components are also present.

2. Chemical Kinetics

Photo-oxidation studies will be extended to lower SO_2 concentrations to provide information for estimating quantum yields for SO_3 in the presence of common flue gas constituents.

ACKNOWLEDGMENTS

The study described in this report has been conducted jointly by GCA Corporation, Riley Stoker Corporation, and the Singco Department of Bolt, Beranek and Newman, Inc. The support and active guidance of the joint sponsors of this program; U. S. Public Health Service, National Air Pollution Control Administration (Contract No. PH-86-67-125), American Petroleum Institute; Bituminous Coal Research, Inc.; and the Edison Electric Institute, is gratefully acknowledged.

We would also like to thank the Boston Edison Co. and the New England Electric System for permission to conduct stack sampling measurements and plume tracer releases at their power station sites.

The contribution of the Riley Stoker Corporation to this program is also acknowledged in the furnishing of significant support during provision of a pilot furnace facility.

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APPENDIX A

EXPERIMENTAL EQUIPMENT, FLIGHT PROGRAM

The aircraft provided under contract with Singco was a Cessna 172. Available payload was 330 pounds and total electrical power generated was 720 watts (at 12 volts). Air samples were drawn into the sampling devices through short (approximately 3-foot) lengths of Teflon tubing attached to the cabin exterior.

The major problem in the design of the sampling system has been to provide the desired instrumentation array within the payload and power constraints. These requirements are summarized in Table A-1. The additional power required will be supplied by aircraft-type storage batteries or by sampling trade-off selections. A 1.5-kilowatt hour battery supply at 130 pounds appears feasible, allowing 80 pounds for cabling and supports.

Preliminary experiments were performed to determine the capacity required to perform the plume sampling. The Casella cascade impactor at 17.5 liters/min, the bubbler train at 3.8 liters/min (two midget impingers in series, and a membrane filter upstream of the impingers), and a membrane filter for fly ash collection at 10 liters/min, require a total flow rate of 31.3 liters/min at a resistance of 10.3 inches Hg. If filter diameter is increased from 1-1/2 to 2 inch diameter, overall sampling system resistance can be lowered to 8.1 inches Hg at 31.3 liters/min. This flow rate can be supplied quite readily by a Gast Model 0521 pump which can deliver 68 liters/min at 10 inches Hg.

Periodic samples for SF_6 analysis were collected in Saran bags by using the ram air flow induced in the 1/4-inch Teflon sampling line attached to the exterior of the cabin.

Pumps for the other sampling equipment use 12 V dc motors except for the Sign-X SO_2 analyzer which operates at 110 V ac. The continuous SO_2 analyzer is furnished with power from a dc-ac inverter (20 pounds).

An electric field mill developed for measurement of atmospheric space charge was evaluated as an alternative method of plume tracking. The Singco field mill consists of a motor-driven six-bladed vane grounded to a housing by silver-graphite brushes. A stator vane, located behind the rotor and insulated from the housing produces the signal. A synchronous motor drives the rotor at 8000 rpm resulting in an 800 cps signal directly proportional to the incident dc electric field. The instrument has maximum accuracy in the 100 to 1000 V/cm range, and sufficient sensitivity to be qualitatively usable in the 20 to 100 V/cm range.

TABLE A-1

AIRCRAFT INSTRUMENTATION

No.		Weight* (lb)	Power (watts)
1	Sign-X SO_2 Analyzer	15	250
2	Impingers	5	30
3	High Volume Sampler	15	400
4	Cascade Impactor	10	100
5	Gas Tracer	1	0
6	Recorder	50	300
7	DC-AC Inverter	20	---
8	Humidiometer	6	---
9	Solar Radiometer	2	---
10	Liquid Water (J&W)	20	60
11	Temperature	2	---
12	Aircraft Radio	---	180
		145	1315

*Does not include mounts or cables

APPENDIX B

INSTRUMENT RESPONSE

In order to facilitate interpretation of the continuously recorded SO_2 concentration data, an elementary analysis of expected instrument response to a number of simple concentration profiles has been prepared as shown in Figure B-1. The analysis was adapted from Middleton's treatment of thermometer lag* and applies rigorously only to an instrument with zero dead time, originally in equilibrium with its surroundings. Short pulses were treated by fitting curve segments. The double ramp (triangle), in particular, is an approximation considered adequate for illustration. The applicable equations are:

(1) Square Pulse (positive or negative)

$$\theta = \theta_e \left[1 - \exp\left(-\frac{t}{\lambda}\right)\right]$$

where θ is the instantaneous instrument reading; θ_e is the peak pulse concentration; λ is the time constant (8 seconds) and t is the time from initiation of the pulse.

(2) Linear Ramp (positive or negative)

$$\theta - \theta_e = -\beta\lambda \left[1 - \exp\left(-\frac{t}{\lambda}\right)\right]$$

where β is the ramp slope in units of concentration/time.

It is clear that considerable profile distortion and concentration underestimation will occur for short pulses which display large concentration gradients. Examples of all the illustrated response events (and many more complex ones) were observed as shown in Figures 5(a) and 5(b).

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*Middleton, W. E. K., and Spilhaus, A. F., Meteorological Instruments, 3rd Edition, University of Toronto Press (1953).

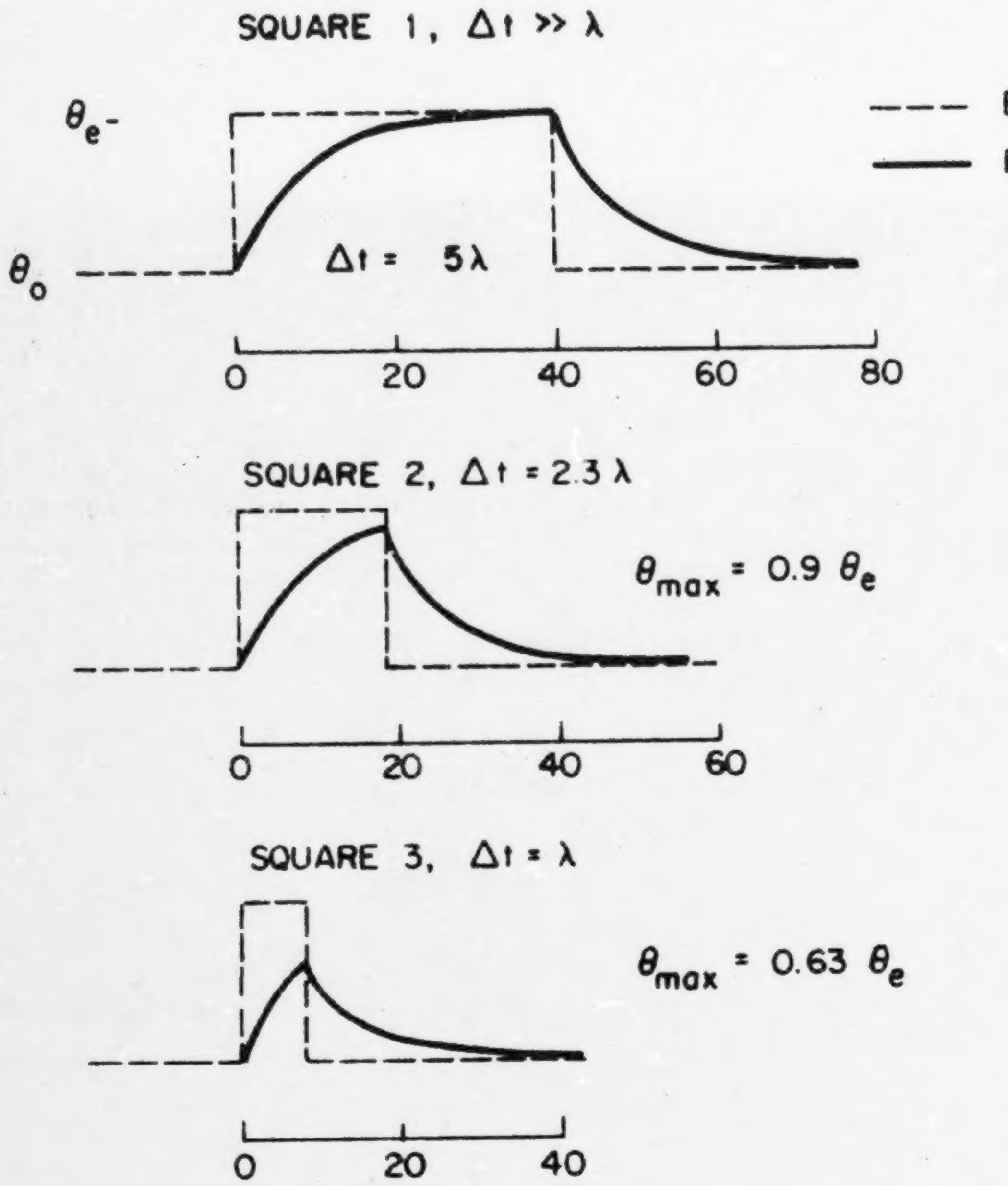

Figure B-1. Calculated instrument response to arbitrary plume profiles (for time constant, λ, eight seconds).

APPENDIX C

INTERPRETATION OF PLUME DATA

Plume "cross-sections" at the distances, headings and times noted in Figure 6 are given in Figure C-1. The recorded profiles at altitude $\geq$ 1000 feet at 1.85 miles are shown in Figure C-2. The apparent plume width for a given profile is defined by the time at which the signal is unambiguously above background. Under flight conditions the minimum detectable signal varied between 1 and 2 percent of full-scale response, or between 1 and 2 pphm "SO_2". The apparent plume width is illustrated in C-2 by the extreme pair of arrows above each trace and is plotted in Figure C-1 as the dashed curves and open circles.

Comparison of the calculated and observed profiles suggests that a conservative, semiquantitative trailing edge correction may be made by selecting that time as the boundary at which the (last) exponential decay has fallen to half-maximum. (The basis of this argument is the comparison of the trapezoid and triangle to the expected Gaussian profile.) This corrected width is marked by the inner arrow above the curves of Figure C-2 and is plotted as the solid line and crosses in Figure C-1. Note, also, that the profiles of Figure C-1 are not geographical, since plume widths were arbitrarily centered. The observed peak concentrations are shown in Figure C-3. It is more difficult to estimate a correction for the recorded peak concentration. We estimate that this may be as much as a factor of two for some of the large gradient peaks (such as No. 18, Figure C-2).

Examination of the plume data reveals that the measurements at the longer distances were terminated at about 1000 feet when no response was obtained. It is not clear, however, after examining the approximate 2000-foot depth of the 1.85 mile profile, whether a change in plume structure occurred or whether a higher altitude plume was missed. Future profiles should not, therefore, be terminated after a single zero response is obtained. There is a hint in the peak concentration profile at 1.85 miles (as shown by the dashed curve, Figure C-3) that a stratified plume was formed, but this depends on the value of a single concentration at 800 feet. This breakup may appear in the plume boundary profile (Figure C-1) which measures the approximate one-tenth peak concentration at 1.85 miles. (At four and at seven miles, the plume boundaries determined are about one-fourth peak concentration as a result of plume dilution at constant instrument sensitivity.)

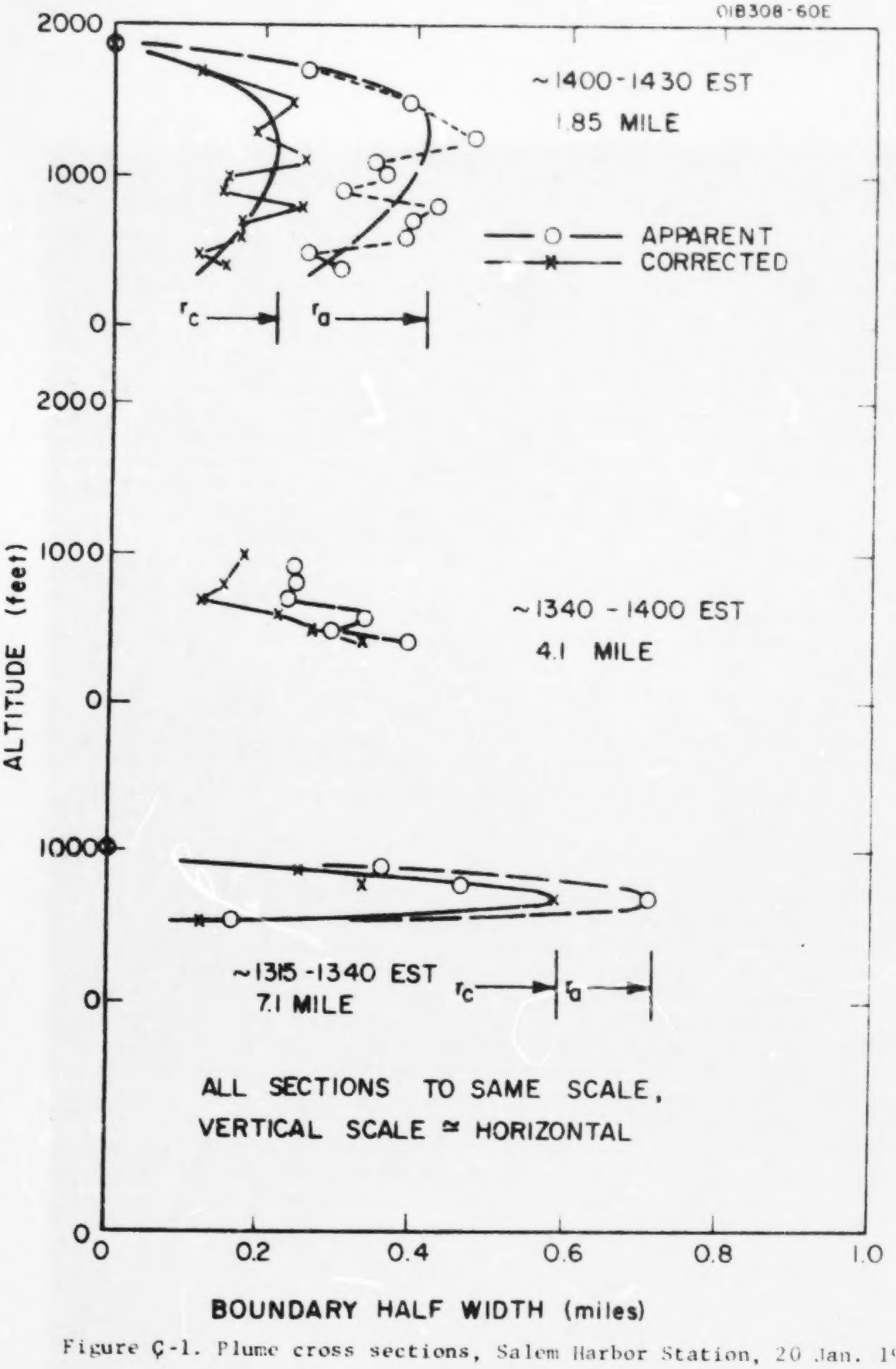

Figure C-1. Plume cross sections, Salem Harbor Station, 20 Jan. 1968.

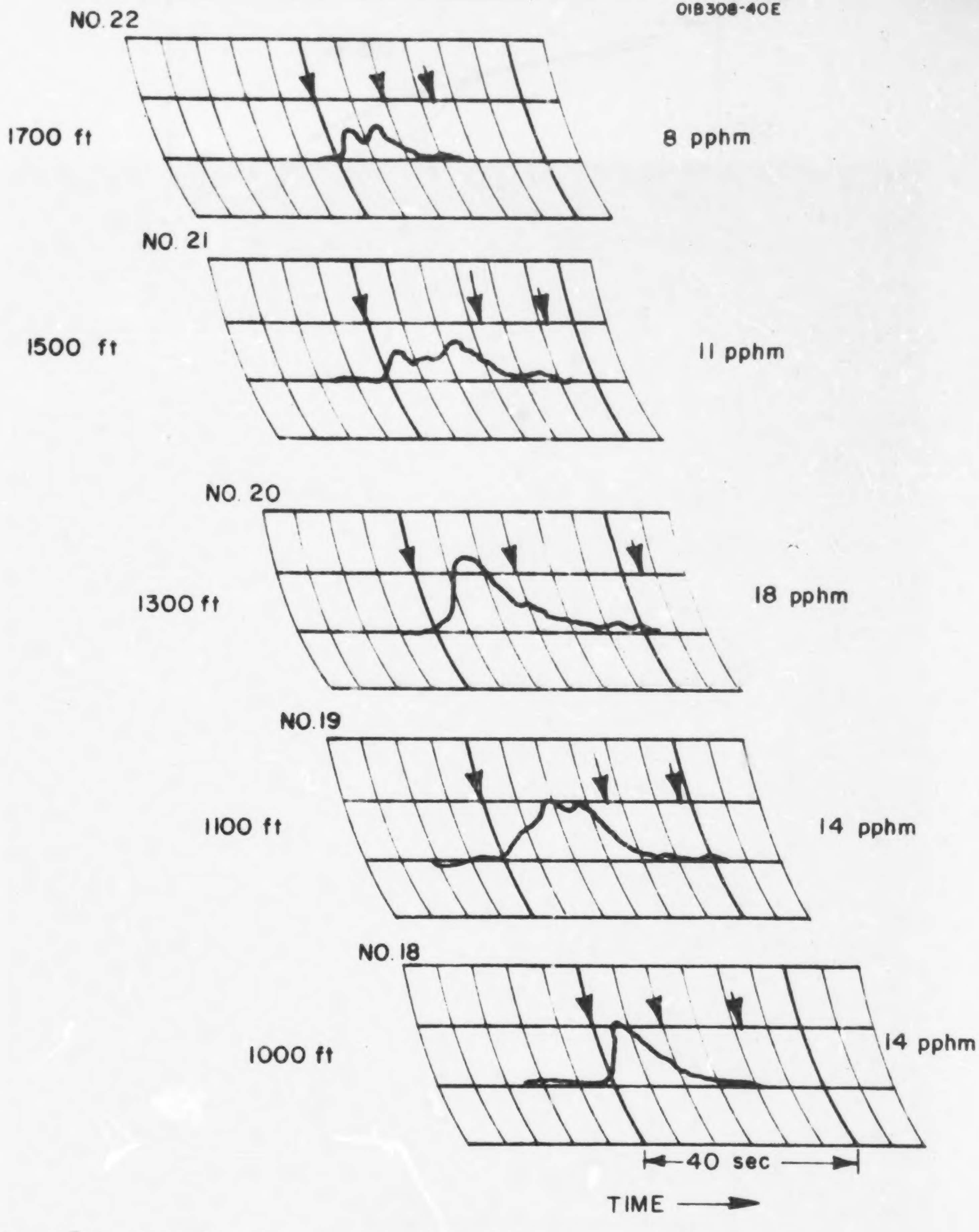

Figure C-2. Recorded plume concentration profiles at 1.85 miles for altitude $\geq$ 1000 feet. Apparent peak SO_2 concentration noted to right. True air speed 80 mph (except No. 18, 90 mph). See Text for explanation of vertical arrows.

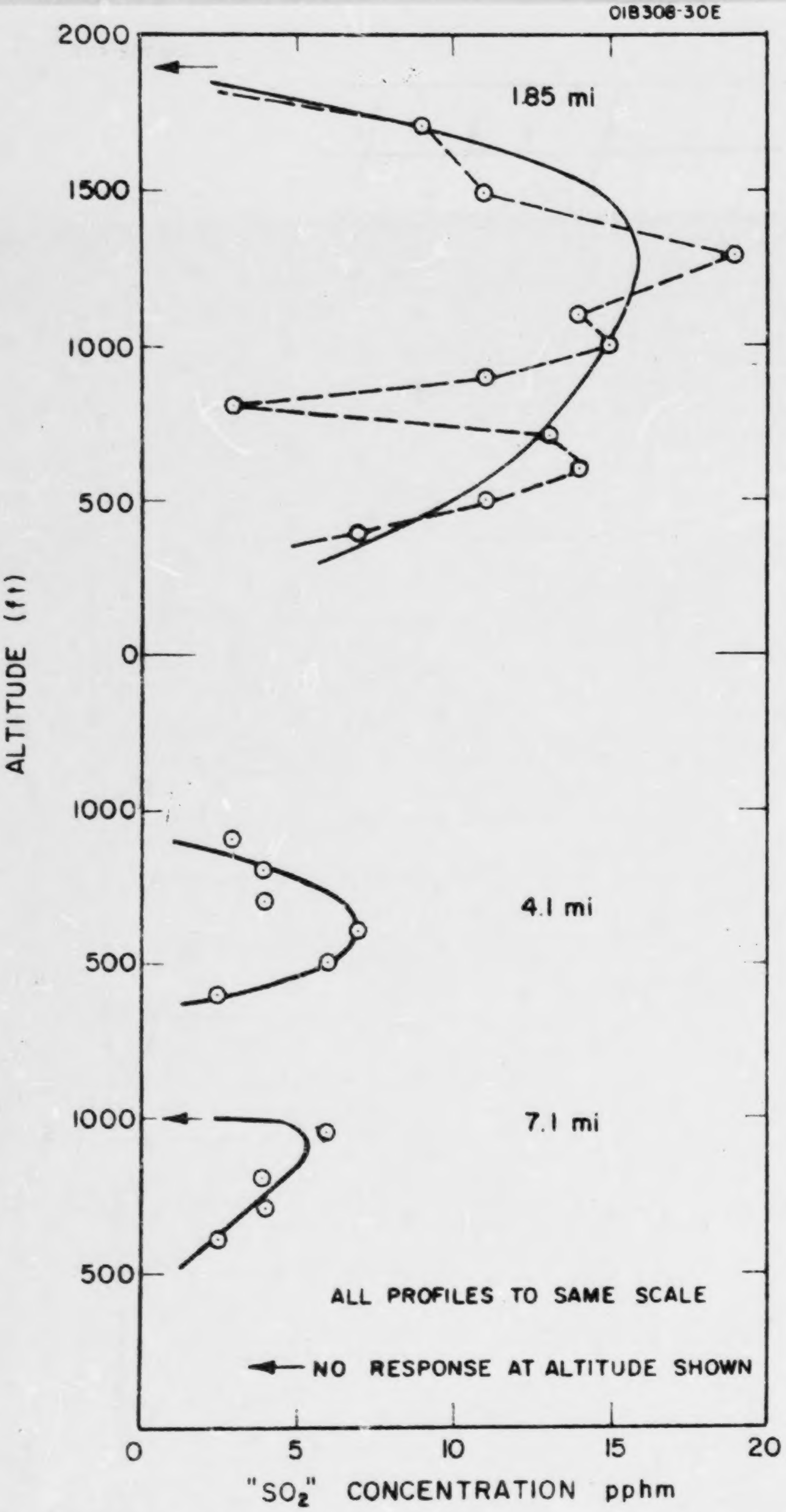

Figure C-3. Apparent peak SO_2 concentration profiles, Salem Harbor, 20 Jan. 1968.

It is apparent that the trailing edge corrections are most significant at short downwind distances (Figure C-1). Even with this instrument, the horizontal structure of the plume is partially discernible (No. 19, 21, 22, Figure C-2). These ambiguities will clearly become less important with the faster instrument.

A problem may be encountered at the very long downwind distances which are of interest in this program, since the seven mile profile, which is of low concentration, represents only about one-half hour decay at 15 miles per hour and little improved sensitivity is to be expected from the fast response instrument. Useful data at long times will be dependent, therefore, upon the frequency of light wind conditions during the next field study phase.

APPENDIX D

DESCRIPTION OF PILOT PLANT

A schematic diagram of the pilot plant facility is shown in Figure D-1. The furnace (Item H) consists of an L-shaped gas path (approximately 3-1/4 feet vertical leg; 2-1/2 feet horizontal leg) with a 9-inch by 9-inch cross section surrounded by about 1 foot of refractory insulating and fire brick. It is designed for a heat release in the range of 50,000 BTU/hr from the combustion of propane, residual oil, or pulverized bituminous coal. Complete design and construction drawings, and operating instructions have been furnished by Riley-Stoker Company.

In operation, the forced draft fan (Q) supplies outside air at positive pressure (3 inches Hg, up to 90 cfm) through flowmeters L, M, and N for primary, secondary, and tertiary combustion air to the gas, oil, or coal burner head. Fuels are supplied from the auxiliary equipment shown in the figure (Items A, B, C, R, S, T, U, X, Y, Z). Combustion occurs downward from the top of the vertical leg of the L-shaped furnace, and gases then proceed along the horizontal leg and up to the finned heat exchanger-air heater (J). Cooled flue gases pass through a cyclone (D), an electrostatic precipitator (E), and then to an irradiated stirred reaction chamber located in the adjacent laboratory. Gases are discharged to the outside by means of the induced draft inductor (F)(driven by a bleed stream from the forced draft fan, (Q). Cooling air for the heat exchanger is drawn from a bleed stream from the forced draft fan (Q) through rotameter (K), passed through the finned exterior of the heat exchanger (J), and either directed outside the building or partially recirculated to the inlet of the forced draft fan (Q) to recover heat when required for proper combustion air temperature.

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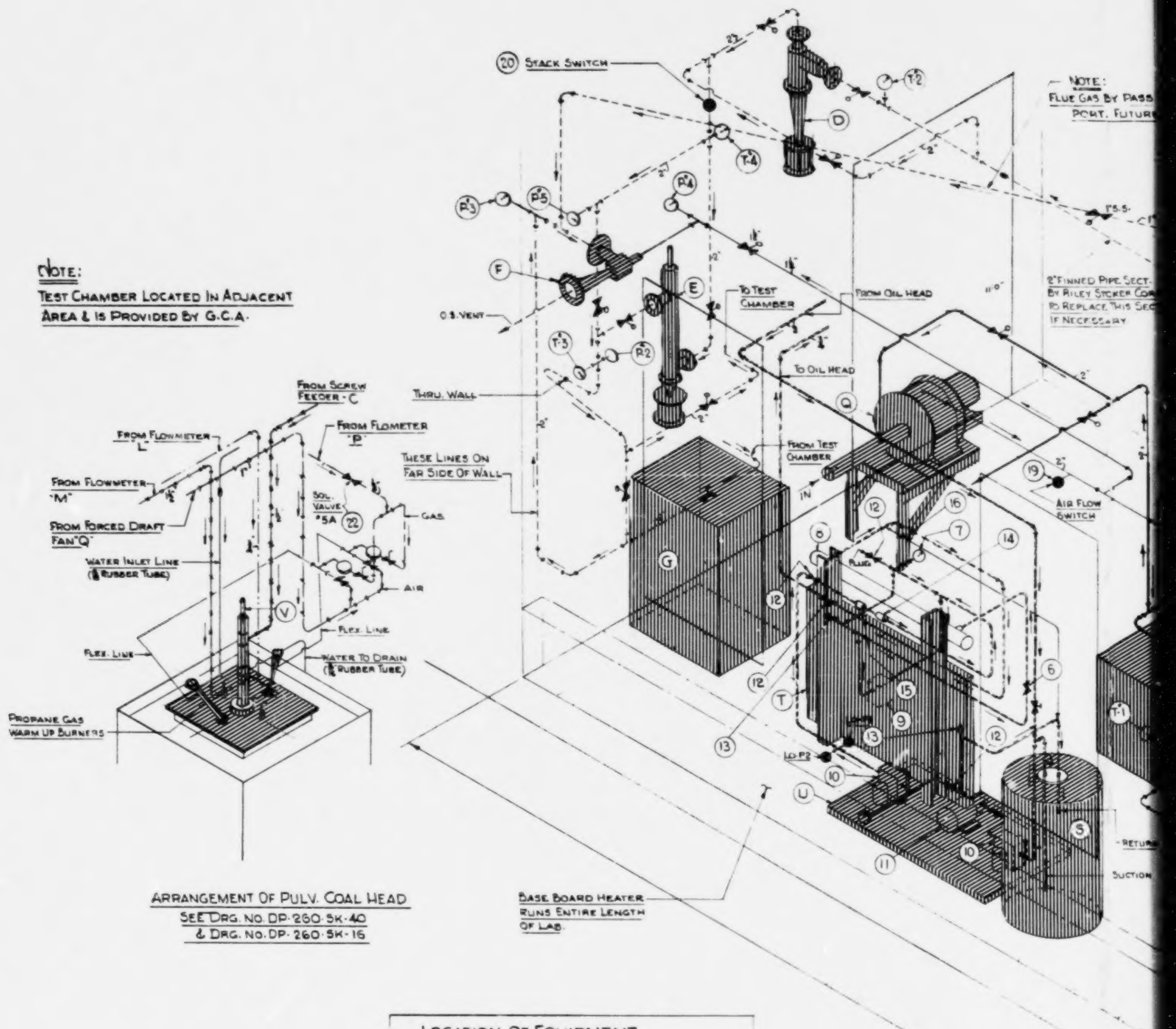
NOTE:
TEST CHAMBER LOCATED IN ADJACENT AREA & IS PROVIDED BY G.C.A.



⑳ STACK SWITCH
D
T-2
T-4
P-3
P-5
P-4
F
E
O.S. VENT
T-3
R2
TO TEST CHAMBER
FROM OIL HEAD
TO OIL HEAD
THRU. WALL
Q
FROM TEST CHAMBER
THESE LINES ON FAR SIDE OF WALL
IN
G
NOTE: FLUE GAS BY PASS PORT. FUTUR
2" FINNED PIPE SECT. BY RILEY STOKER COR TO REPLACE THIS SEC IF NECESSARY
1"S.S.
11'-0"
2"
1½"
19
AIR FLOW SWITCH
12
16
7
14
8
PLUG
6
15
9
13
T
LO-P2
10
U
11
S
T-1
RETUR
SUCTION
FROM SCREW FEEDER - C
FROM FLOWMETER "L"
FROM FLOMETER "P"
FROM FLOWMETER "M"
FROM FORCED DRAFT FAN "Q"
SOL. VALVE #5A ㉒
GAS
AIR
WATER INLET LINE (⅜ RUBBER TUBE)
V
FLEX. LINE
WATER TO DRAIN (⅜ RUBBER TUBE)
PROPANE GAS WARM UP BURNERS
BASE BOARD HEATER RUNS ENTIRE LENGTH OF LAB.
26'-0" INS.

ARRANGEMENT OF PULV. COAL HEAD
SEE DRG. NO. DP-260-SK-40
& DRG. NO. DP-260-SK-16

BASE BOARD HEATER RUNS ENTIRE LENGTH OF LAB.

KEY-PLAN

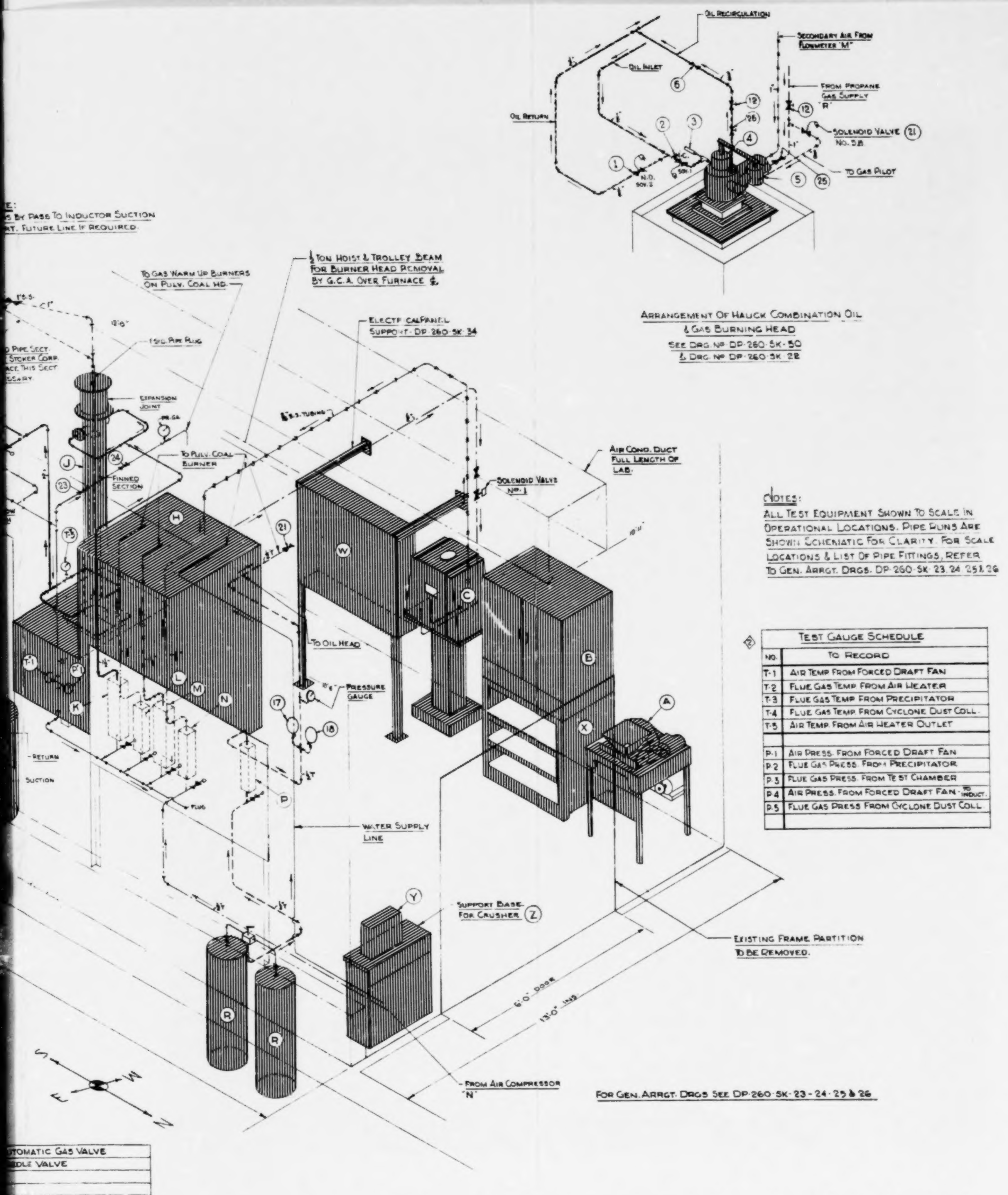
PROPANE GAS	— — — —
PROPANE AIR	——•——⁄——
DRAFT AIR	————————
PRIMARY AIR	— — · — · —
SECONDARY AIR	—•—•—•—•—
TERTIARY AIR	—— ·· —— ·· ——
COOLING AIR	━━━━━━━━
FLUE GAS	- - - - - - - -
PULV. COAL	━•━•━•━•━
OIL	▬ ▬ ▬ ▬
VALVE	——⋈——

LOCATION OF EQUIPMENT

Nº	DESCRIPTION
A	PULVASIZER
B	DRYING OVEN
C	SCREW FEEDER
D	CYCLONE DUST COLLECTOR
E	ELECTRO PERCIPITATOR
F	JET COMPRESSOR - (INDUCTOR)
G	POWER PACK 40 KV
H	FURNACE
J	AIR HEATER
K	FLOW METER - COOLING AIR TO STACK
L	FLOW METER - TERTIARY AIR
M	FLOW METER - SECONDARY AIR
N	FLOW METER - PRIMARY AIR
P	FLOW METER - PROPANE GAS
Q	FORCED DRAFT FAN
R	PROPANE SUPPLY TANKS - OUTSIDE BLDG
S	OIL SUPPLY TANK - 55 GAL.
T	HEAT & CIRC UNIT - SINGLE HEAT, SINGLE PUMP - OIL
U	SINGLE OIL PUMPING UNIT
V	PULVERIZED COAL BURNER
W	ELECTRICAL PANEL
X	OVEN BASE & BAG STORAGE CABINET
Y	COAL CRUSHER
Z	SUPPORT BASE FOR CRUSHER

LOCATION OF OIL BURNER EQUIP. & CONTROLS

Nº	DESCRIPTION		
1	SOLENOID VALVE - NORMALLY OPEN		
2	SOLENOID VALVE - NORMALLY - CLOSED		
3	HEATER ELEMENT		
4	MICRO - REGULATING VALVE - OIL		
5	PROPORTIONING VALVE - GAS		
6	CHECK VALVE		
7	PRESSURE GA. & VALVE		
8	OIL HEATER		
9	CIRCULATION PUMP		
10	OIL STRAINER		
11	SUPPLY PUMP		
12	GATE VALVE		
13	RELIEF VALVE	25	AUTOMATIC G
14	OIL REGULATOR	26	NEEDLE VALV
15	OIL FILTER		
16	THERMOL RELIEF VALVE		
17	GAS LOW PRESSURE SWITCH		
18	GAS HIGH PRESSURE SWITCH		
19	AIR FLOW SWITCH		
20	STACK SWITCH		
21	SOLENOID VALVE Nº 5B		
22	SOLENOID VALVE Nº 5A		
23	BALL CHECK VALVE		
24	SOLENOID VALVE Nº 4		


Oil Recirculation
Secondary Air From Flowmeter "M"
Oil Inlet
From Propane Gas Supply "R"
Oil Return
Solenoid Valve (21) No. 5B
To Gas Pilot
N.O. SOV. 2
SOV. 1
(1)
(2)
(3)
(4)
(5)
(6)
(12)
(25)
(26)
Arrangement Of Hauck Combination Oil & Gas Burning Head
See Drg. No DP-260-SK-50 & Drg. No DP-260-SK-28
E:
S By Pass To Inductor Suction
AT. Future Line If Required.
To Gas Warm Up Burners On Pulv. Coal Hd.
½ Ton Hoist & Trolley Beam For Burner Head Removal By G.C.A. Over Furnace ℄.
Electrical Panel Support - DP-260-SK-34
1" S.S.
1" Std. Pipe Plug
D Pipe Sect.
Stoker Corp.
ace This Sect
ssary.
Expansion Joint
Pr. Ga.
⅜" S.S. Tubing
To Pulv. Coal Burner
Finned Section
Air Cond. Duct Full Length Of Lab.
Solenoid Valve No. 1
To Oil Head
Pressure Gauge
Water Supply Line
Return
Suction
Plug
Support Base For Crusher (Z)
Existing Frame Partition To Be Removed.
6'-0" Door
13'-0"
From Air Compressor "N"
For Gen. Arrgt. Drgs See DP-260-SK-23-24-25 & 26
S
W
E
N
H
J
W
C
B
A
X
K
L
M
N
P
Y
R
R
T-1
P-1
T-5
(17)
(18)
(21)
(23)
(24)
utomatic Gas Valve
edle Valve

Notes:
All Test Equipment Shown To Scale In Operational Locations. Pipe Runs Are Shown Schematic For Clarity. For Scale Locations & List Of Pipe Fittings, Refer To Gen. Arrgt. Drgs. DP-260-SK-23, 24, 25 & 26

Test Gauge Schedule	
No.	To Record
T-1	Air Temp From Forced Draft Fan
T-2	Flue Gas Temp From Air Heater
T-3	Flue Gas Temp From Precipitator
T-4	Flue Gas Temp. From Cyclone Dust Coll.
T-5	Air Temp. From Air Heater Outlet
P-1	Air Press. From Forced Draft Fan
P-2	Flue Gas Press. From Precipitator
P-3	Flue Gas Press. From Test Chamber
P-4	Air Press. From Forced Draft Fan - To Induct.
P-5	Flue Gas Press From Cyclone Dust Coll.

Figure D-1. GCA-Riley combustion gas generating pilot plant, isometric view, after Dwg. No. DP-260-SK-41-4, Riley Stoker Corp., Worcester, Mass. (4-25-68) for GCA Technology Division, Bedford, Mass.

B

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TABLE D-1

NO. 6 OIL ANALYSIS

Viscosity SSF at 122 degrees F--------------160

Sulfur % ----------------------------------2.25

B.S. % ------------------------------------ 0.2

Water by Distillation % ------------------- 0.3

Humble Oil
Lab.

Specific Gravity at 60 degrees F ----------- 0.959

BTU/lb ------------------------------------ 18,530

Sulfur % --------------------------------- 2.3

Riley Stoker
Lab.

APPENDIX E

IRRADIATED REACTION CHAMBER - DESIGN FEATURES

E.1. MODIFICATIONS TO THE COMMERCIAL NOR-LAKE FREEZER UNIT (Figure E-1)

(1) Cooling coils of copper instead of aluminum.

(2) A 3/4-horsepower motor and compressor unit.

(3) A United Electric Model E32N temperature control to replace the standard unit for a control range of -150°F to +150°F.

(4) A triple layer glass door.

(5) An 8-inch diameter ultraviolet transmitting port.

(6) Six plastic pipe nipple access holes.

(7) Chamber pressure checked at +5 inches water pressure and a latching dog installed to prevent leakage.

(8) Front surface mirrors (2 feet by 4 feet) in contact with the two side walls.

In addition, further modification will be made during the first test series, including:

(1) Lining of the aluminum interior with "Trifoil" Teflon coated aluminum foil.

(2) Shielding of the temperature transducer.

(3) Installation of a mixing fan.

E.2. SOLAR SIMULATOR

Solar simulation* in the reactor may require some adjustment. The normal solar flux on 1 m^2 is about 1400 watts. A simulator which can generate a beam of about 500 watts is contemplated for initial use. In a real plume at the concentrations of principal interest, the absorption of sunlight per foot of travel of the beam is small and the plume is effectively uniformly illuminated through its thickness. Therefore, chamber

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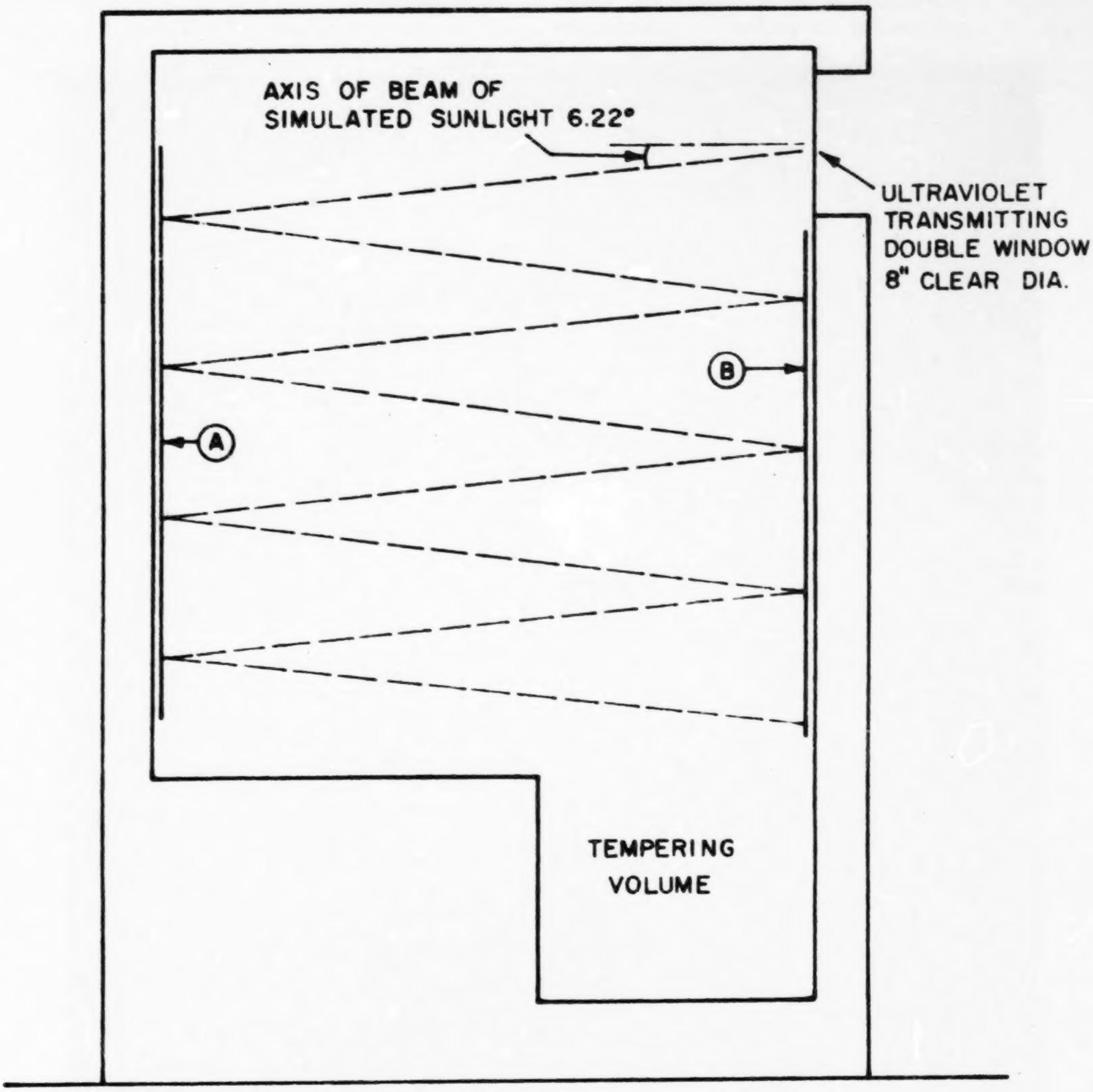
*Genarco Model ME4 Solar Simulator

018300-10E


AXIS OF BEAM OF
SIMULATED SUNLIGHT 6.22°
ULTRAVIOLET
TRANSMITTING
DOUBLE WINDOW
8" CLEAR DIA.
B
A
TEMPERING
VOLUME

NOTE: MIRROR DIMENSIONS 24" x 40"
INSIDE BOX DEPTH 26"
WIDTH 46" and 20"
HEIGHT 50" and 66"
SCALE 1" = 10"
A, B PLANE FRONT SURFACE ALUMINIZED MIRRORS

Figure E-1. Irradiated reaction chamber.

illumination at the required level is obtained by folding the beam within the reactor to provide a pathlength equal to the volume of the reactor divided by the area which can be illuminated at one solar constant with the beam entering the reactor. Additional consideration is being directed to the possible use of a light source with higher flux in the wavelength region of interest (3100Å).

E.3 PERKIN-ELMER MODEL 357 IR SPECTROPHOTOMETER

The instrument cell has a pathlength which can be varied from 1.25 to 10 meters and can be operated at pressures up to 10 atmospheres. The original CsBr windows have been replaced with Irtran II windows which are not attacked by water vapor or other materials. The wavelength range is now limited by the long wavelength cutoff of Irtran II which is about 14 microns. Nevertheless, the concentrations of most air pollutants can be determined within the 2 to 4-micron wavelength range. A Cole-Palmer peristaltic pump cycles the chamber air through the measuring cell at 1 liter/min and returns it to the chamber.

APPENDIX F

APPARATUS AND PROCEDURES PHOTOLYSIS STUDIES

F.1. FLOW REACTOR

The flow reactor employed for measuring the quantum yields of SO_3 is shown in Figure F-4. A removable window was provided so that it could be cleaned after each run to eliminate one of the difficulties encountered in previous SO_2 photolysis, i.e., fogging in the windows and reduction of the incident flux. Matheson anhydrous grade sulfur dioxide, 99.98 percent minimum purity, was bubbled through concentrated sulfuric acid at atmosphere pressure (to remove traces of SO_3 in the SO_2), metered with a calibrated flow meter, and passed into the reaction vessel. At a flow rate of 2.5 milliliters per second, and with total absorption of photon flux within 1 centimeter of the window surface, total residence time of SO_2 in the beam was about 1 second.

F.2. SAMPLING AND ANALYSIS

The SO_3 formed was collected in distilled water or an 80-percent isopropanol-water mixture. It has been assumed that SO_3 proceeds to $SO_4^=$ with 100 percent conversion efficiency. The excess dissolved SO_2 was removed at the conclusion of a run by flushing the solution with nitrogen for 25 to 45 minutes. The barium chloranilate procedure was used for sulfate analysis. The nonzero background concentration was observed in this system in the absence of radiation because of residual absorbence due to the dissolved SO_2 and some conversion of dissolved SO_2 and some conversion of dissolved SO_2 to SO_3. The photochemically formed $SO_4^=$ was calculated from the difference between background and total absorbence as shown in Figure F-5.

When a second bubbler was placed in series with the first, SO_3 could not be detected in the downsteam vessel after 30 minutes of irradiation with the unfiltered mercury arc indicating that, within detection sensitivity, all the SO_3 produced (approximately 3.2 micromoles) was collected in the first bubbler.

F.3. UV SOURCE

A Hanovia mercury utility lamp cooled by a blower was employed as the light source for the photolysis. Cooling increases the ultraviolet flux by at least an order of magnitude compared to uncooled operation. The apparent relative intensities of the spectral lines in the discharge were obtained using a half-meter Seya monochromator with an EMI-9514 photomultiplier viewing a sodium salicylate-coated glass plate (wavelength shifter). The monochromator is equipped with a Bausch and Lomb 1200 line per millimeter gold-coated grating (50-centimeter radius of curvature) blazed at about 1200Å. The fluorescence efficiency of sodium salicylate is constant throughout this spectral region (2500 to 3100Å) thereby eliminating photomultiplier corrections. The efficiency of a similar grating in the same geometry has been measured from 1200 to 6000Å (Ref. 25). Using these values to correct the apparent relative intensities of the mercury lines, the actual intensity distribution from the lamp is obtained from 2537 to 3130Å.

F.4. UV SOURCE CALIBRATION

The photon flux of the lamp was measured with the ferrioxalate actinometer described by Hatchard and Parker (Ref. 30). The actinometer solution (0.006N ferrioxalate) was irradiated through a 1-inch diameter Suprasil quartz plate cemented to an opening in the side of the vessel. This geometry is effectively the same as that of the reaction vessel. Owing to the sensitivity of the ferrioxalate actinometer to visible light, the photon flux from the lamp was determined at 2537 and 3130Å using Baird narrow band interference filters for visible light exclusion.

Transmission characteristics for the various filters and windows used for the photochemical measurements are shown in Figure F-7. For the 2537Å photolysis of SO_2, the quartz window was used in conjunction with the 2537Å filter. The 3130Å filter was used for actinometry only since the low transmission through the filter would require long exposure times. In the 3100Å photolysis of SO_2, the quartz window was replaced by a pyrex window. This window transmits most of the radiation > 3000Å and eliminates the contribution of the 2537Å mercury line. Although long wavelength mercury lines at 3341, 3650, 4358Å, etc. are also transmitted by this window, they are not absorbed by the SO_2. The active mercury lines passed by the pyrex window are 2967, 3021, 3125, 3130, and 3131Å. Actinometry with the 3130Å filter was employed to derive the absolute intensities of the 3125 and 3131Å lines, but the intensities of the 2967 and 3021Å lines were obtained from the corrected intensity distribution of the lamp (above). Since the corrected intensities of the mercury emission lines are known from 2537 to 3130Å, the light flux can be calculated at 3100Å from the actinometry at 2537Å. The results obtained in this manner were in good agreement (within 10 percent) with the values obtained with the 3130Å actinometry.

The light flux transmitted by the 2537Å filter was found to be $(2.72 \pm 0.15) \times 10^{15}$ quanta/second. The purex filter passed $(8.4 \pm 0.5) \times 10^{14}$ quanta/second of radiation between 2967 and 2121Å.

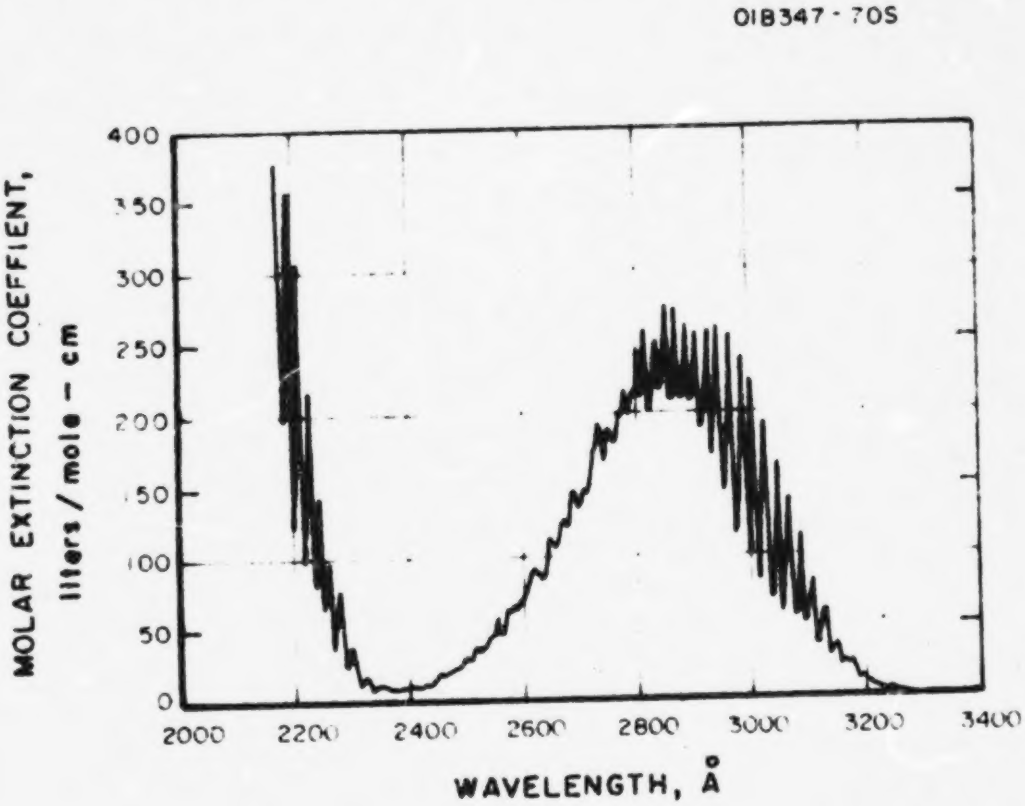


Figure F-1. The absorption spectrum of SO_2 gas

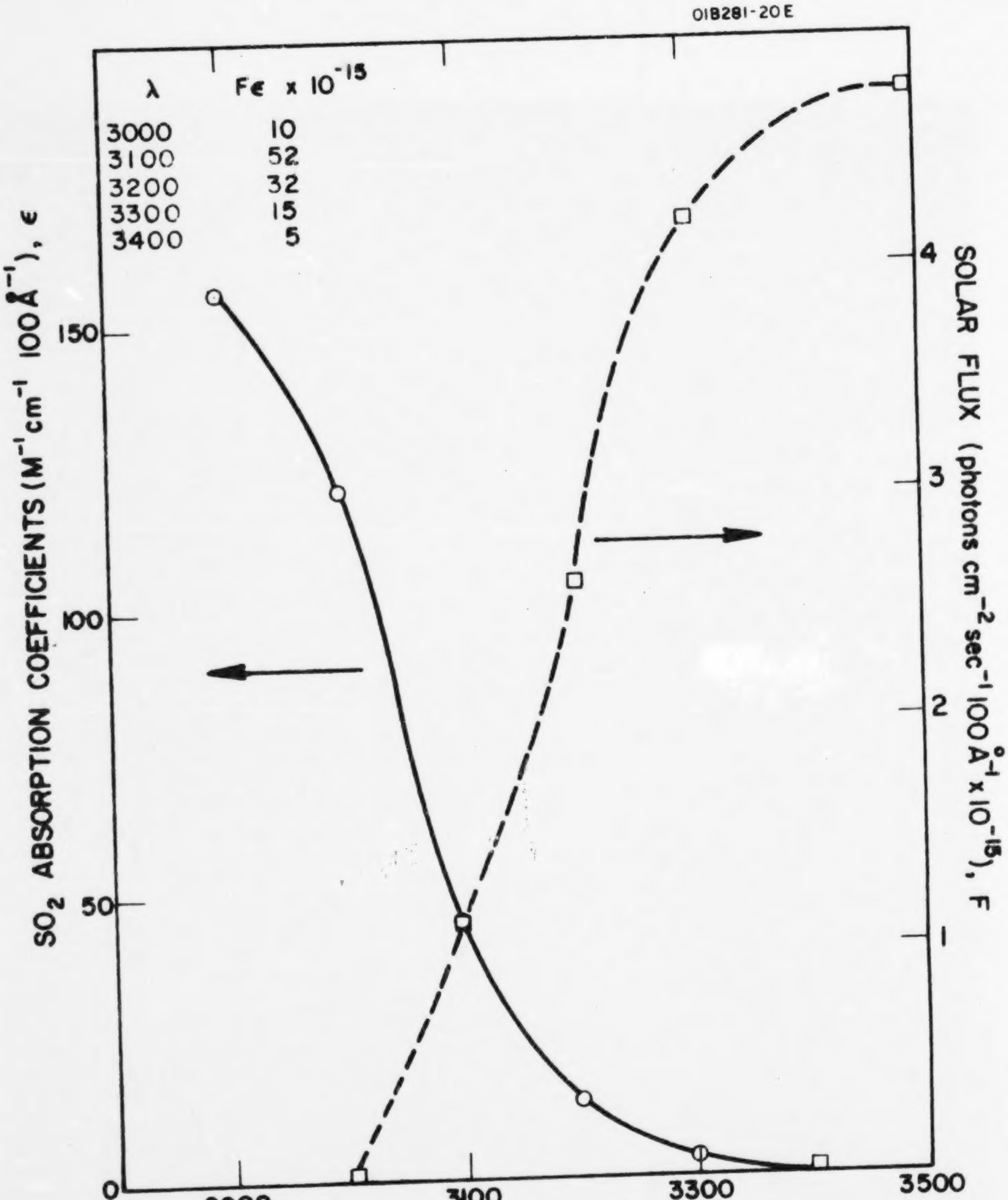


Figure F-2. Approximate absorption coefficients for SO_2 and solar flux at the zenith angle of 0^o as a function of wavelength

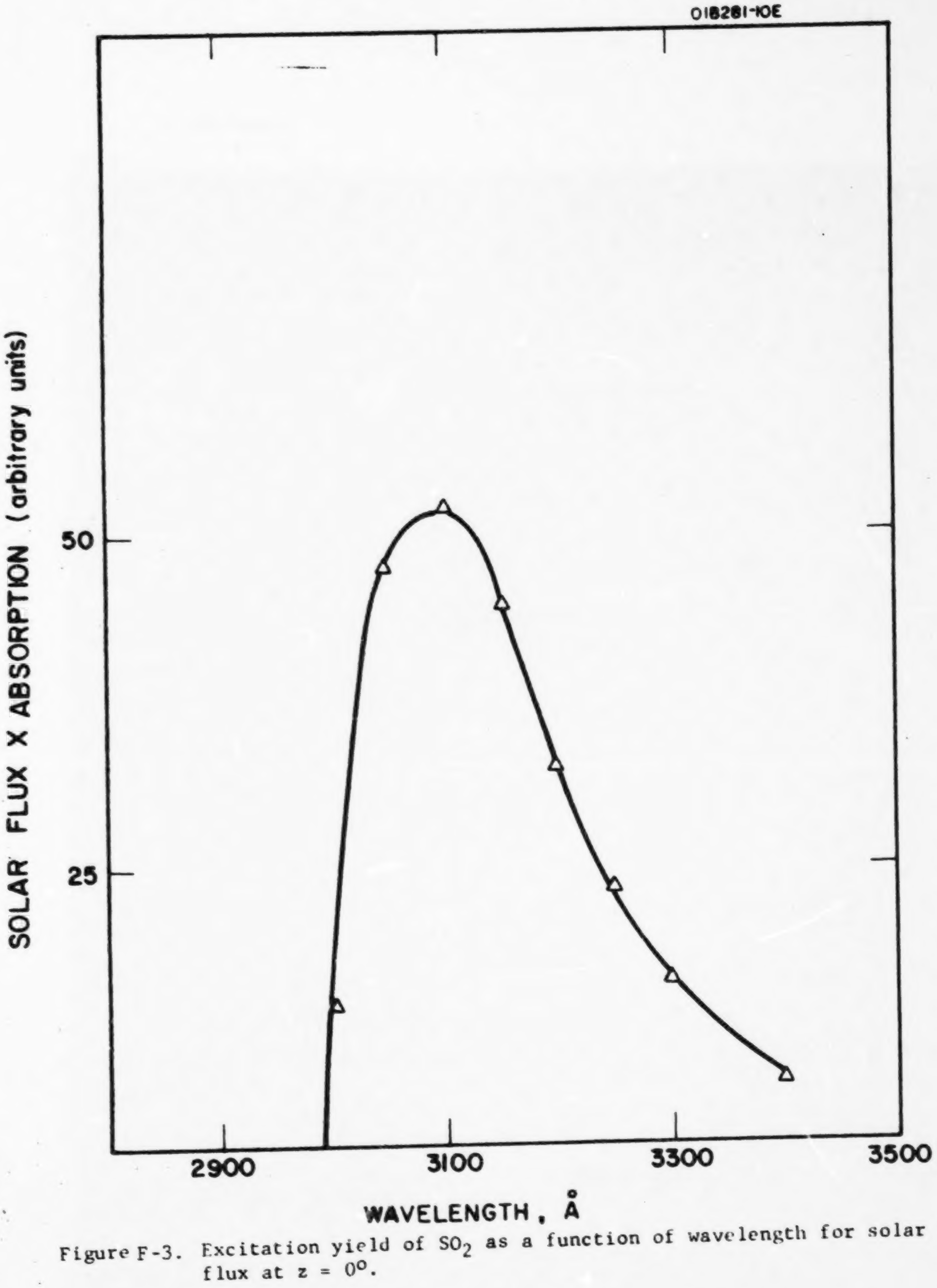


Figure F-3. Excitation yield of SO_2 as a function of wavelength for solar flux at $z = 0^o$.

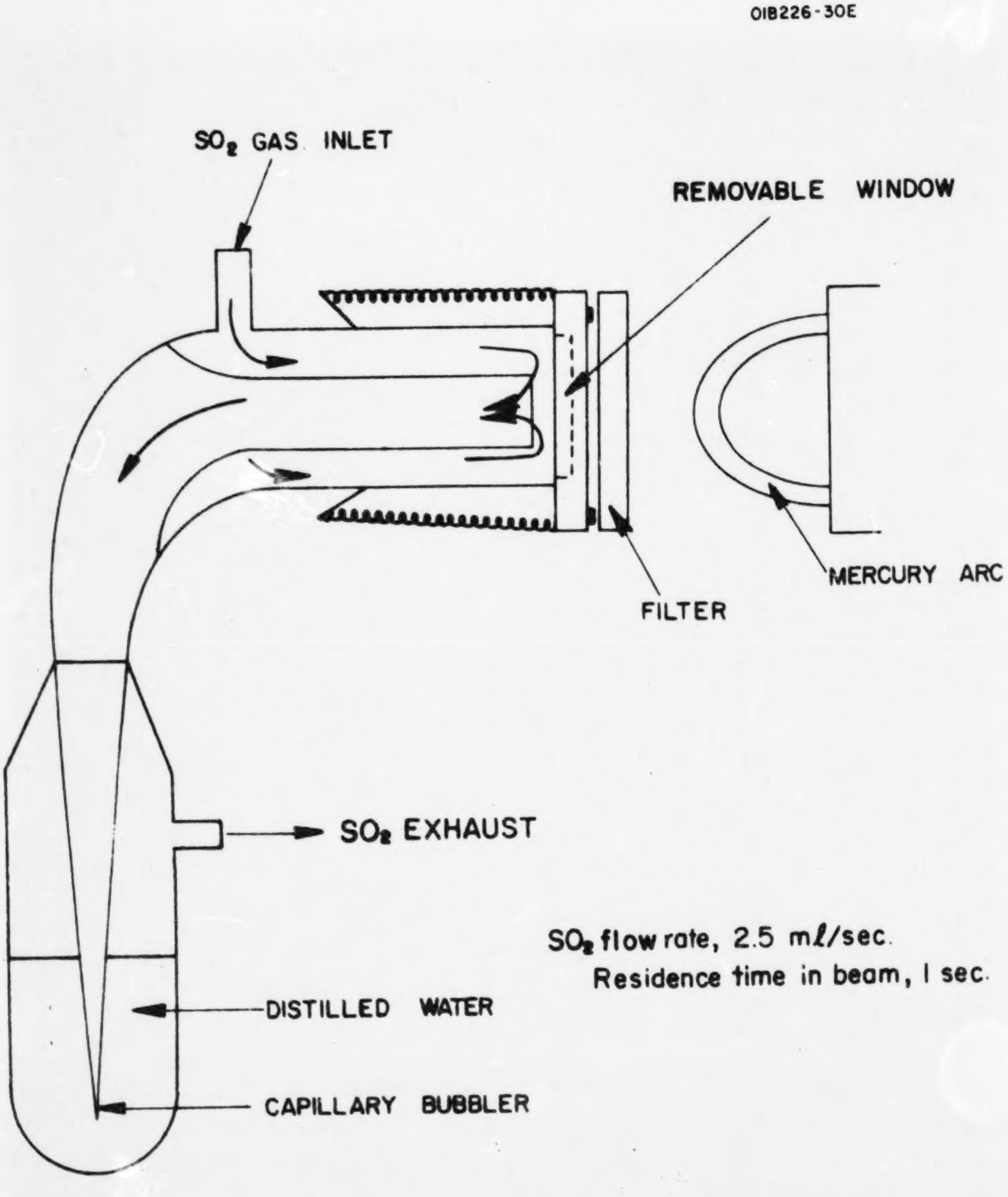

01B226-30E
SO_2 GAS INLET
REMOVABLE WINDOW
MERCURY ARC
FILTER
SO_2 EXHAUST
SO_2 flow rate, 2.5 mℓ/sec.
Residence time in beam, 1 sec.
DISTILLED WATER
CAPILLARY BUBBLER

Figure F-4. Photochemical flow reactor.

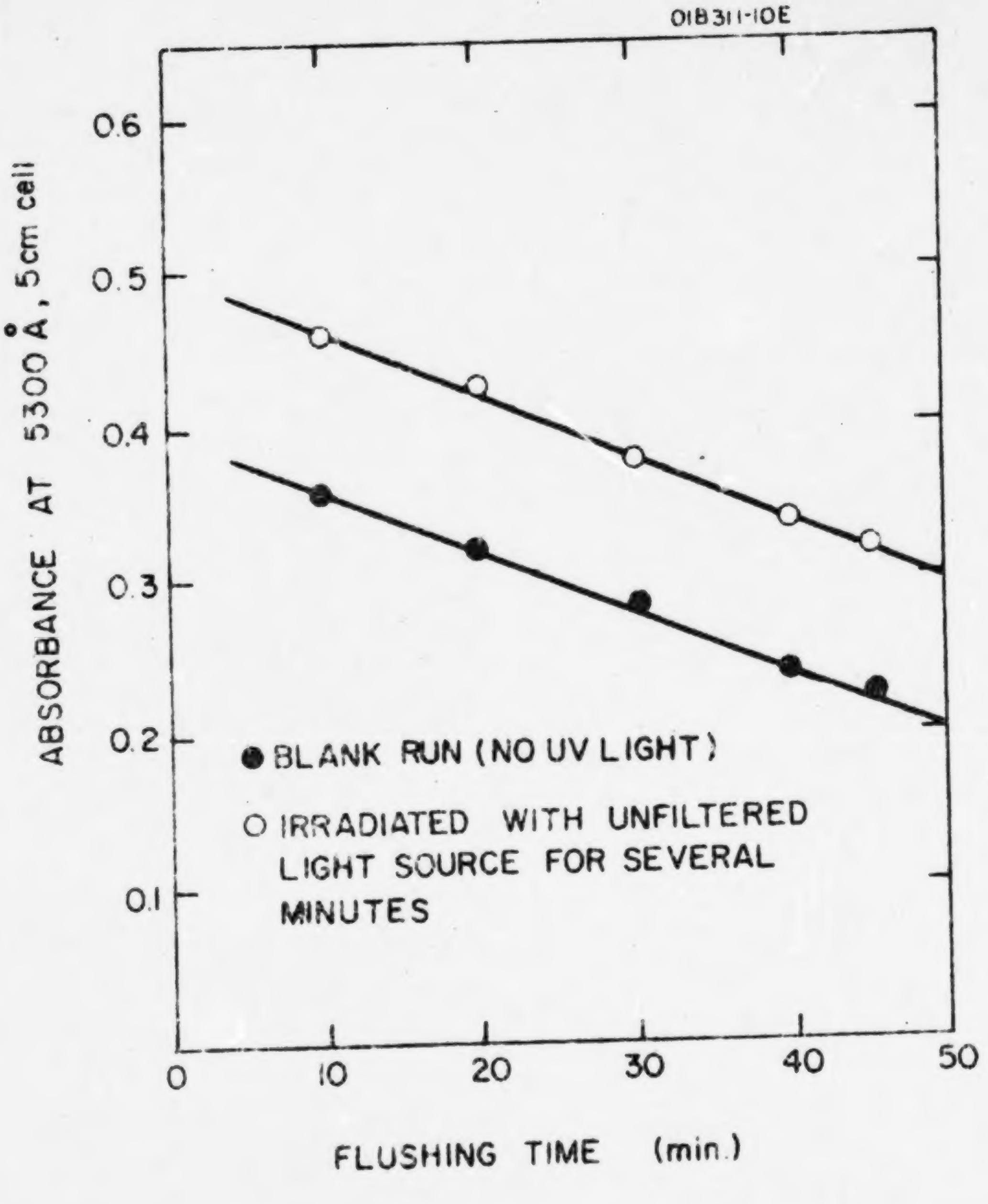


Figure F-5. Sulfur dioxide photolysis and background yield.

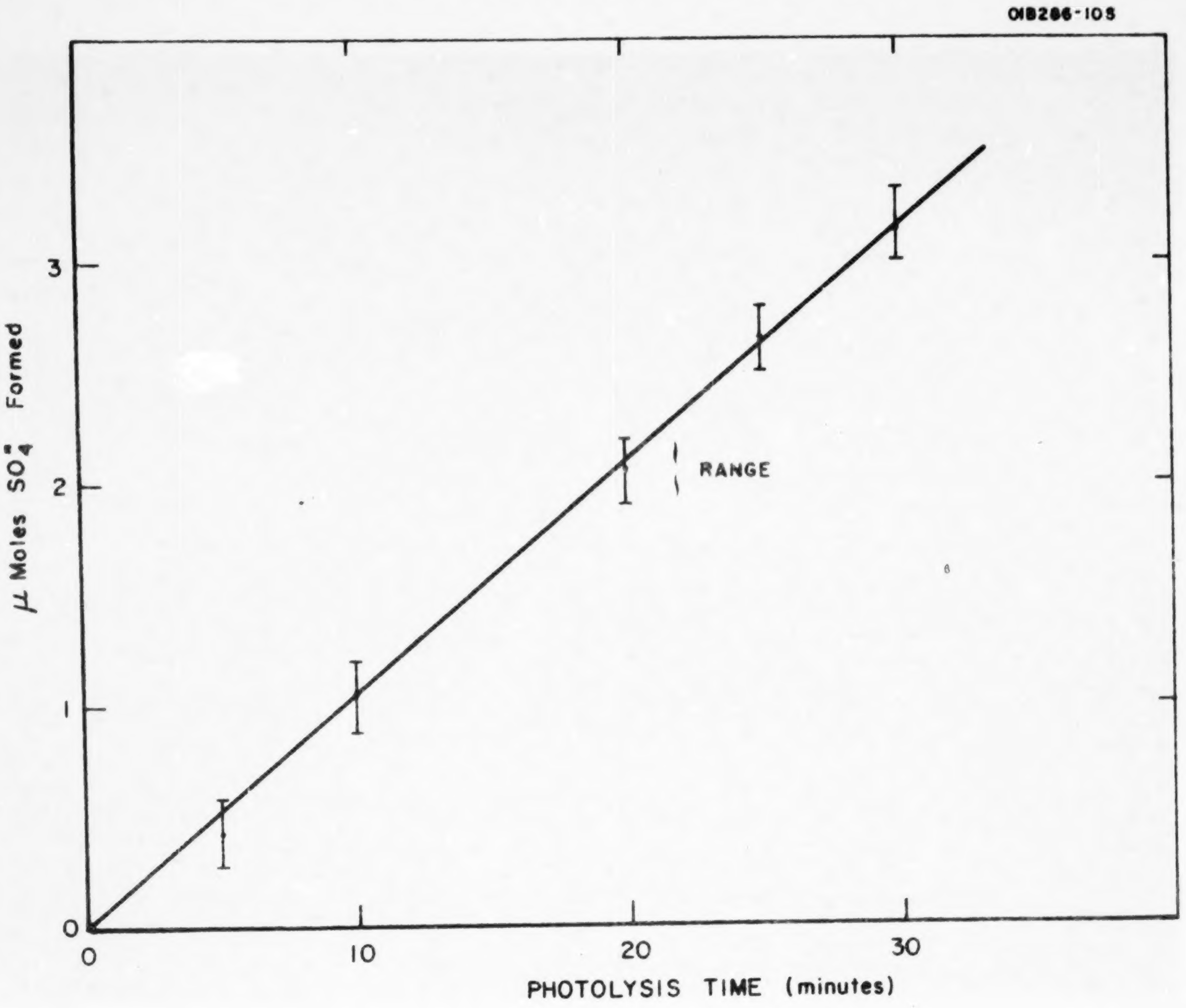


Figure F-6. Photolysis of SO_2 with unfiltered Hg arc.

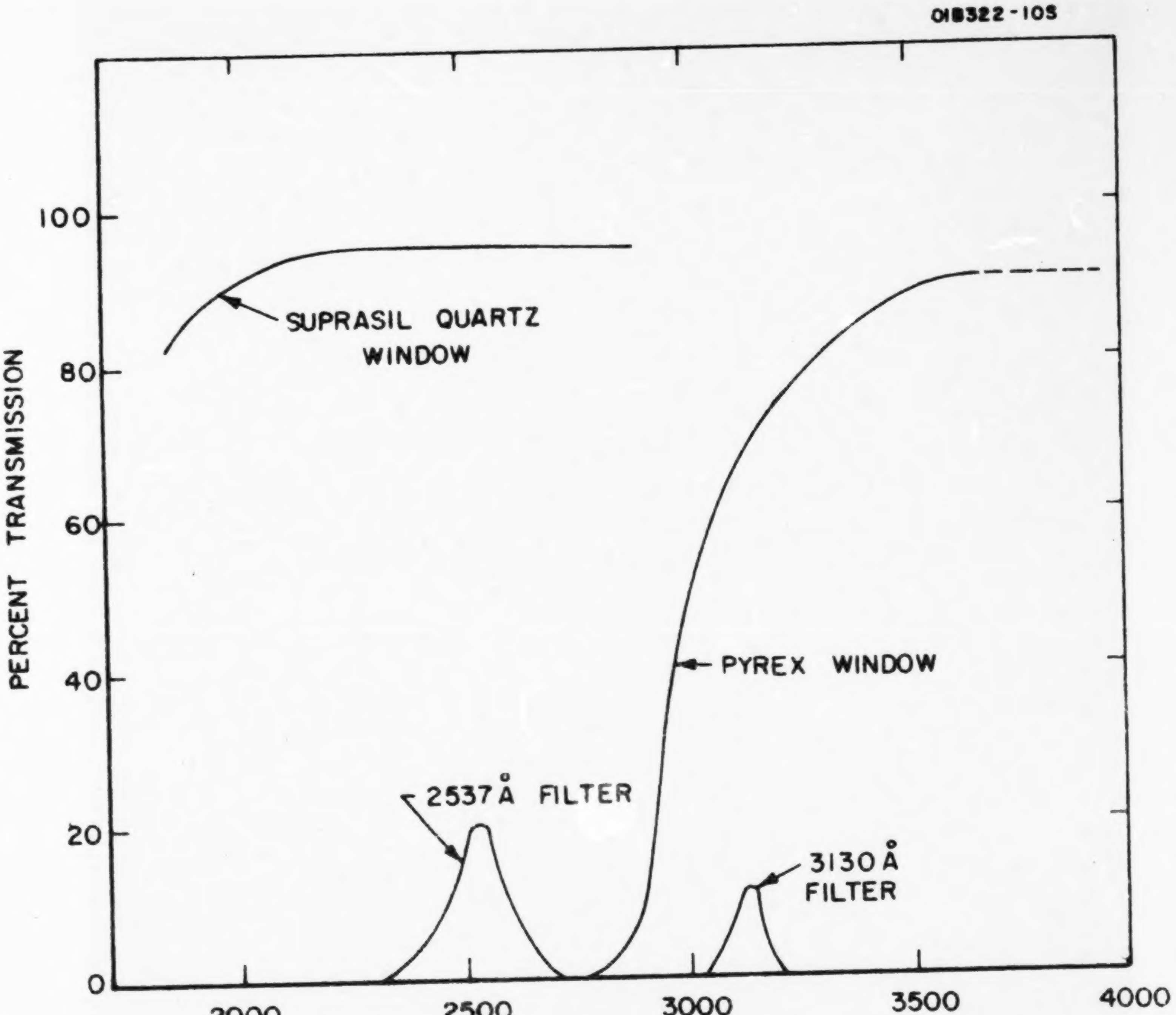


Figure F-7. Transmission characteristics of windows and filters used in SO_2 photolysis.

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